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AN INVESTIGATION INTO THE EFFECTS OF
AN HERBICIDE ON HISTORIC MASONRY
MATERIALS

Catherine Camille Dewey

A THESIS

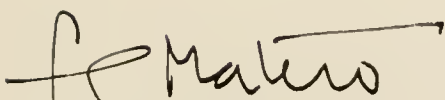
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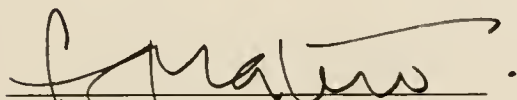
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Nature had come into her own again and little by little, in her stealthy insidious way had encroached upon the drive with long tenacious fingers. The woods, always a menace in the past, had triumphed in the end.

-Daphne du Maurier, Rebecca

Chapter One: Introduction

Through nature and neglect comes the downfall of monuments. Structures that have survived for hundreds or thousands of years gradually perish under neglect. In addition to many other deterioration mechanisms, neglect can lead to invasive plant growth. As the desire to preserve our cultural heritage grows ever stronger, man has developed numerous solutions to extend the life of historic structures. One such solution is the use of chemical treatments, ranging from consolidants to biocides. Among these, herbicides have a prominent place in the battle against unwanted vegetation in our culturally important sites.

While the effectiveness of many herbicidal products has been tested time and again, rarely has the question of herbicidal effects on masonry been examined. In this fight against encroaching vegetation, are the applied chemicals actually harming the very sites we are trying to save? Considering the extensive use of chemical vegetation control, this topic is sorely underrepresented in the

conservation field.¹ Although the use of herbicides and biocides against growth is a common conservation intervention, very few products have been tested or developed specifically for use on historic masonry materials. Many herbicide products are “borrowed” from agriculture and landscape applications. Standardized tests to evaluate the effect of any treatment, intended or not, should be developed to insure the conservation axiom of “do not harm.”

Over the past few decades, the amount of literature produced that is concerned with biodegradation and biodeterioration has grown extensively.² A large amount concentrates on the degradation caused by vegetation and the factors contributing to plant growth. The *Biodeterioration Research Series* published in association with the Biodeterioration Society covers many aspects of the deterioration caused by growth.³ In nearly every conservation-related symposium or meeting, a session is dedicated to biological growth on one material or another. With these types of venues as a beginning, the interest in biological growth and its effects on cultural heritage blossomed. Publications such as *Biology in the Conservation of Works of Art* by G. Caneva, M. P. Nugari and O. Salvadori (1991) is the first comprehensive compilation on the types of biological growth, the types of deterioration they cause, and the various methods by which they might be controlled.

¹ Literature survey on Canadian Heritage Information Network, www.chin.gc.ca, using keywords “biocide” or “herbicide” and “masonry” resulted in only 13 references.

² Literature survey on Canadian Heritage Information Network, www.chin.gc.ca, using keywords “biodeterioration” or “biodegradation” resulted in hundreds of references.

Most of the published literature is concerned with deterioration caused by microflora such as algae and lichens. This type of growth is often overlooked as a cause of deterioration especially when it occurs on masonry, and is considered only when cleaning is undertaken. Its significance on masonry is often overshadowed by environmental parameters, inherent structural defects, and the influence of soluble salts. Biological growth, more often than not, is removed because of its unsightliness, not its harmfulness. It is generally not a priority in a conservation plan. However, attention must also be given to vascular plants, those having roots, as mechanisms of damage. The intrusion of higher plants is often viewed as a maintenance problem rather than one for a trained conservator. However, higher plants can cause not only extensive mechanical damage but chemical damage as well. The growth of higher plants is especially problematic at archaeological sites such as Ankor Wat in Thailand, Pompeii in Italy, Chersonesos in Ukraine, and numerous other sites throughout the world. As greater recognition of the serious damage caused by plants grows, the challenge of effectively dealing with the problem increases. Although the use of herbicides to effectively eliminate growth has increased, few researchers have examined the question of how continued herbicidal treatment will affect masonry. This thesis was developed through a strong interest on the part of researchers

³ *Biodeterioration Research I-4* (New York : Plenum Press, 1987-1994).

and site managers to determine the long-term usefulness and potential damage of herbicides on historic masonry.

In the late seventies, James Fearn of the National Bureau of Standards, was requested by the National Park Service to investigate the question of herbicidal effects on masonry.⁴ This was the first published investigation into whether the chemical affected masonry or not. He examined the existing literature and drew conclusions based on various publications on herbicides. After examining the types of masonry that would be most affected and the types of herbicides then available, conclusions were based primarily on chemical and material knowledge. Some tests were conducted at the Mississippi Test Facility of the National Park Service at Bay St. Louis, Mississippi. Brick and mortar samples were soaked in two different herbicides for one week and tested for various properties including porosity and compressive strength. No change was recorded. This publication raises the question of chemical effects caused by herbicides on masonry, and attempts to provide guidelines for the selection of an herbicide. It further suggests a testing program to evaluate visible change with herbicides.

The next major study of the herbicidal effects on historic masonry was prepared by Linda Cook as a Master's thesis in Historic Preservation at

⁴ James E. Fearn, *The Effects of Herbicides on Masonry* (Springfield: National Technical Information Service, 1978).

Columbia University entitled “The Effects of Herbicides on Masonry: Products, Choices, and Testing”(1989). After a comprehensive examination of chemical control methods for unwanted vegetation, a laboratory testing program was executed. By examining various physical and chemical changes to the masonry units before and after testing, the author concluded that the cumulative use of herbicides can cause mechanical damage and staining to stone and mortars. The current thesis attempts to extend this research into the present and to further qualify the effects of herbicides on masonry.

Other recent and useful research was conducted by Rachel D. Wakefield and Melanie S. Jones.⁵ An innovative method was developed to analyze the potential dissolution caused by biocidal interaction with the masonry, more specifically, sandstone. After the stone was crushed and washed, it was soaked in a biocide. The stones were crushed “to ensure that all readily exchangeable ions and small particulates were removed to minimize sources of contamination by mineral components not directly interacting with the biocidal applications.” The residues produced by this method were then analyzed using Scanning Electron Microscopy, X-ray Diffraction and Energy Dispersive X-ray Analysis.

Two articles by M.P. Nugari and others were informative and useful as guides in designing a testing program. In “Methodological Evaluation of Biocide

⁵ Rachel D. Wakefield, and Melanie S. Jones, “Some Effects of Masonry Biocides on Intact and Decayed Stone” in *Eighth International Congress on Deterioration and Conservation of Stone, Berlin, 30 Sept. - 4 Oct. 1996: Proceedings*, edited by Josef Riederer (Berlin: S. N., 1996).

Interference with Stone Materials,”(1993)⁶ evaluation of secondary effects of two different biocides was carried out. Testing included water absorption by capillarity, chromatic variation, Scanning Electron Microscopy and Energy Dispersive X-ray Spectrometry. Although more reasonable, a water absorption by capillarity test was not used in the testing program of this thesis because of the variable shape of some of the samples. A water absorption test by total immersion was used instead. Assessment of chromatic variation was also used in this testing program. More advanced methods of analysis did not fit into the scope of this thesis, but their results were helpful in serving as a guide to the possible outcome of this testing program. A second article entitled “Test Methods for Comparative Evaluation of Biocide Treatments,”⁷ concentrated more on the efficacy of the treatment on retarding growth, but also examined some secondary effects on the stone, including chromatic variation.

The final and most recent document helpful in this research was “Biodeterioration of Stone: An Evaluation of Possible Treatments and Their Effects with Special Reference to Marble Statuary at Cliveden, Germantown, Pennsylvania”(1997), a Master's thesis from the University of Pennsylvania by Karen Fix. The author examined both the effects and the effectiveness of

⁶ M.P. Nugari, P. Palleschi, and D. Pinna, “ Methodological Evaluation of Biocidal Interference with Stone Materials- Preliminary Laboratory Tests” in *Conservation of Stone and Other Materials: Proceedings of the International RILEM/UNESCO Congress Held at the UNESCO Headquarters, Paris, June 29-July 1, 1993*, edited by M.J.Thiel (London: E. & F. N. Spon, Ltd., 1993).

⁷ M.P. Nugari, M.S. D’Urbano and O. Salvadori, “Test Methods for Comparative Evaluation of Biocide Treatments” in *Conservation of Stone and Other Materials: Proceedings of the International*

biocides on marble. Tests such as measurement of surface roughness, water drop absorption, hygroscopicity, as well as more advanced analysis were included. Due to the coarse, porous nature of the sandstone samples in the current research, neither surface roughness measurements nor the water drop absorption test were appropriate. A similar test for hygroscopicity was used.

Through the above-mentioned studies, it has been established that porosity, permeability and color are likely to be affected by the use of certain chemical controls.⁸ The introduction of additional soluble salts will also be examined. The aim of this thesis is to evaluate the effects of a commonly used commercial herbicide, Round-up® at different concentrations to appraise long-term cumulative effects. The masonry materials chosen were two weathered units, and two fresh units to evaluate potential effects on weathered as well as unweathered samples. The materials were characterized before and after treatment to evaluate any changes in mineralogy, porosity, weight, color and chemical properties, such as pH and salt formation. An attempt was made to identify effects that may affect the durability of the stone such as mineralogical changes, increases in soluble salts, and increases in water absorption capacity. It is hoped that this thesis might provide corroborative and new information about

RILEM/UNESCO Congress Held at the UNESCO Headquarters, Paris, June 29-July 1, 1993, edited by M. J. Thiel, (London.: E. & F. N. Spon, Ltd., 1993).

⁸ M.P. Nugari, P. Pallecchi, and D. Pinna.

the effects and applicability of herbicides to our cultural heritage and a stepping stone to further research on the chemical effects of biocides on stone.

Chapter Two: Damage Caused by Higher Plants

Biological growth in its many forms – from microbacteria to trees – can cause substantial damage to historic monuments. Algae, lichens and higher plants, such as ferns, gymnosperms and angiosperms, compose the classes between these. Higher plants are classified by their reproductive processes as well as by their growth period, such as annuals, biennial and perennials. The various forms often co-exist with growth generally occurring in succession, firstly with microbiological growth, shifting to lichens then to minute plants and finally woody plants, shrubs and even trees.

All masonry monuments, especially recently excavated archaeological sites, are subject to biological growth. Higher plant forms are one of the most immediately damaging types of biological growth. Masonry joints and cracks provide numerous crevices for plants to take root. Once the site is excavated, although carefully cleaned, soil is often left in cracks and crevices providing a fertile ground for seeds. Vegetation and damage are more likely to occur the longer the site or building is exposed due to the accumulation of soil and the breakdown of materials creating voids where water can collect or seeds are deposited.¹ Growth can appear on both horizontal and vertical surfaces. When conditions are favorable, plants can grow almost anywhere: near foundations, on

¹Teresa M.L.S. Mouga, and Maria Teresa F Almeida, "Excavated Monuments as Environment for Plants Conimbriga, Portugal: A Study Case" in *The Third International Symposium on the Conservation of*

walls, in gutters and even between walls. For successful growth, plants need a source of nutrients, a source of light and a suitable climate. Nutrients can come in the form of minerals extracted from soil, stones, mortars, or even organic substances from previous plant growth on a substrate.² In order to photosynthesize, plants favor a certain wavelength, intensity and amount of light. Certain climatic parameters, such as temperature, rainfall and seasonal variations, also play a significant role in plant growth. Continuously warm temperatures and moist air promote more extensive plant growth than cooler temperatures and dryer air. Higher temperatures increase the speed of chemical reactions that take place in plants thereby increasing their growth.³ The amount of water and the period of wetness also affect the growth of the plant.⁴ The more accessible the water and the longer it remains, the more conducive is the climate to vegetation.

Damage from plants comes in the form of direct, often short-term physico-mechanical effects and long-term chemical effects, yet vegetation can also have indirect influences on the durability of masonry such as hiding previous deterioration and altering the microclimate. The most visible and well-known damage caused by plant growth is mechanical. Plant growth occurs most often

Monuments in the Mediterranean Basin, edited by Vasco Fassina, Heinrich Ott and Fulvio Zezza (Venice: Soprintendenza ai beni artistici e storici di Venezia, 1994), 326.

² G. Caneva and O. Salvadori, "Biodeterioration of Stone" in *The Deterioration and Conservation of Stone: Notes from the International Venetian Courses on Stone Restoration*, edited by Lorenzo Lazzarini and Richard Pieper (Paris: UNESCO, 1988), 187.

³ Caneva and Salvadori, 189.

where particle matter has accumulated, where mortar is altered or lost, and at contact angles where materials might accumulate.⁵

Herbaceous growth on stones depends on the ability of the plant to extract from the stone what it needs for survival. Brick structures with a mortar binding, or stones with vulnerable compounds, such as calcium carbonate, some feldspars, mica, and marl tend to be more easily damaged by plant growth.⁶ These stones consist of potential nutrients for vegetation and are more prone to attack from plants. Calcium is one mineral consumed by plants as a nutrient as described below. Granites provide nutrients through certain feldspars and micas, and sandstones and bricks with marl.⁷ The surfaces of more compact stones are less likely to be directly affected by vegetation because of their lower porosities which do not retain excessive amounts of moisture.⁸ Vegetation favors more porous building materials as they provide a foothold as well as retain more water when wet.

⁴ Caneva and Salvadori, 189.

⁵ S. Garcia-Murillo, and S. Martin-Perez, "Presence, Distribution and Bioalteration Phenomenon Associated to Higher Plants in the Pamplona Cathedral (Spain)" in *Eighth International Congress on Deterioration and Conservation of Stone, Berlin, 30 Sept. - 4 Oct. 1996: Proceedings*, edited by Josef Riederer (Berlin: S. N., 1996), 655.

⁶ K.R. Srinivasan, "Vegetation on Monuments," *Ancient India* (1949): 108.

⁷ Srinivasan, 108.

⁸ Srinivasan, 108.

Mechanical Damage

While the above ground elements cause little direct damage other than erosion by rubbing stems or leaves,⁹ and discoloration from fallen and decayed organic matter, the root system can be quite harmful. Plants with large root systems are obviously the most damaging to structures allowing the development of numerous places for mechanical and chemical deterioration.¹⁰



Figure 1: Small plants growing in joints

⁹ Garcia-Murillo, 658.

¹⁰ Sowden A. M., *The Maintenance of Brick and Stone Masonry Structure* (London, E. & F. N. Spon, 1990), 217.

As the plant grows, the roots lengthen and thicken exerting a great deal of force on the unyielding stone around them.¹¹ Plants exert this pressure axially, as the root lengthens, or radially, as the root thickens when growth is inhibited.¹² The pressure of growing roots has been measured to be as high as 19 atm or 278 psi.¹³

Some consequences of root infiltration include dislodgment of facing stone and plasters, and the formation of new cracks or the enlargement of existing cracks.¹⁴ Removal of a weak substrate or mortar is also a function of plant damage.¹⁵ Penetrating roots can also enlarge pores that act as a starting point for freeze/thaw and other mechanical damage.¹⁶ Large woody plants that are intertwined with the wall also pose a serious threat. If the plant is removed by man or nature, the wall can be pulled apart. Roots also retain moisture contributing to lower mechanical strength displayed by many masonry materials when wet.

Chemical Damage

In addition to the physical damage caused by penetrating roots, the chemical reactions of roots cause a more subtle damage. A root is the

¹¹ Srinivasan, 107.

¹² E.M. Winkler, *Stone in Architecture: Properties and Durability*, Third Edition (New York: Springer-Verlag, 1994), 226.

¹³ Winkler, 226.

¹⁴ Srinivasan, 107.

¹⁵ Garcia-Murillo, 658.

hypogean organ where the plant extracts nutrients from the soil and through which the plant exudes waste products.¹⁷ Chemical weathering occurs in the rhizosphere, which is the interface between the root and the substrate. In a study by Caneva and Altieri (1988), root acidity of certain plants ranged between 5.3 and 6.4 pH.¹⁸ Because of the high concentration of hydrogen ions surrounding the roots of plants, the pH is low.¹⁹

The process of chemical weathering, as related to plant activity, has been investigated and described by Keller and Frederickson. The root surface is “enveloped by hydrogen ions which are chemically aggressive to minerals due to a greater chemical potential energy arising from their high electrical charge per unit volume.”²⁰ As the root advances into a void of the rock, this characteristic destroys tangential mineral compounds. The hydrogen ions invade the fractured lattice at the crystal boundary and displace sodium, calcium or potassium, which are absorbed by the root as nutrients.²¹ As the plant removes these minerals and replaces them with hydrogen ions at the surface, it restores the original

¹⁶ G.G. Fisher, “Weed Damage to Materials and Structures,” *International Biodeterioration Bulletin* 8, no 3 (1972): 101.

¹⁷ G. Caneva and A. Altieri, “Biochemical Mechanisms of Stone Weathering Induced by Plant Growth” in *The Sixth International Congress of Stone Deterioration and Conservation, Proceedings, Torun, 12-14 September, 1988*, edited by J. Ciabach (Torun: Nicholas Copernicus University Press Department, 1988), 33-34.

¹⁸ C. Saiz-Jimenez, “Biodeterioration of Historic Buildings and Monuments” in *Eighth International Congress on Deterioration and Conservation of Stone, Berlin, 30 Sept. - 4 Oct. 1996: Proceedings*, edited by Josef Riederer (Berlin: S. N., 1996), 599.

¹⁹ N.D. Keller and A.F. Frederickson, “The Role of Plants and Colloid Acids in the Mechanisms of Weathering,” *American Journal of Science* 250 (1952): 596.

²⁰ Keller and Frederickson, 597.

²¹ Keller and Frederickson, 597-598.

concentration of hydrogen ions.²² The replacement of sodium, calcium or potassium ions by H^+ ions destroys the stability of the lattice because of the difference of coordination between the H^+ ions and the metal cations.²³ Hydrogen ions are easily exchanged for nutrients because of their small size and their high-energy chemical properties arising from a large charge for a small particle.²⁴ Carbonate materials tend to be more susceptible to weathering because of their sensitivity to acid attack.

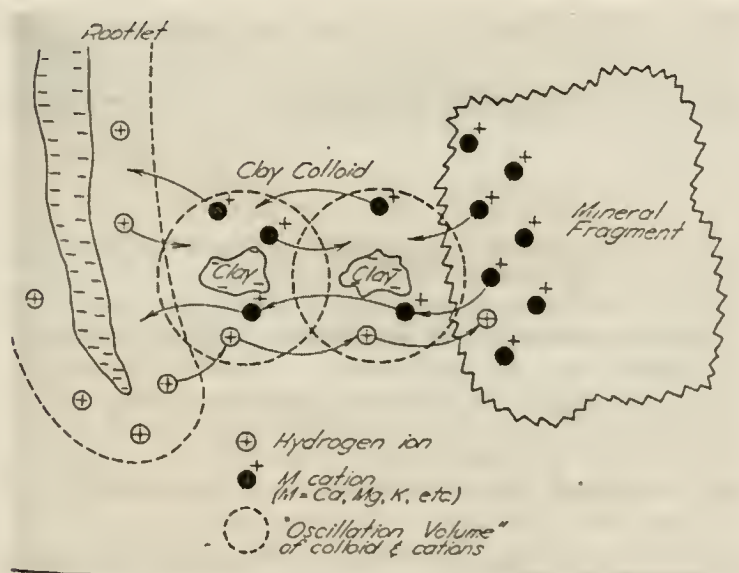


Figure 2: Diagram of hydrogen-mineral exchange between plant roots and mineral (reprinted from Keller and Frederickson)

²² Keller and Frederickson, 598.

²³ Keller and Frederickson, 599.

²⁴ Keller and Frederickson, 607.

As the plant uses nutrients from the stone for its survival, it releases products that have a detrimental effect to the stones. Oxalic, carboxalic and sulfuric acids may be produced by higher plants.²⁵ The deteriorating actions of these acids include mineral etching, chelating and salt formation.²⁶ Chelation occurs with the “trapping” of larger ions such as Ca^{+2} , Fe^{+2} , and Mg^{+2} , into soluble compounds which can leach out of the stones upon wetting.²⁷ By using the nutrients from the stone, the plants act as a chelating agent in which metal ions are taken into a void of an organic ring structure in which calcium is tightly held.²⁸ This leads to mineral disassociation and deterioration of the stone.²⁹ The minerals that are affected by these actions are those commonly found in stone and containing ions such as calcium, magnesium, iron, phosphorus, silicon, and potassium among others.³⁰ While both acids and chelating agents deteriorate masonry, chelating can occur at a wider pH interval than acids.³¹

Another type of chemical deterioration can result from the formation of humus from the decomposition of decayed plants leading to the production of humic acids which can act as solvents.³² Humus in turn provides nutrients for

²⁵ K. K. Jain, “Biodeterioration of Stone: Mechanisms Involved” in *Recent Advances in Biodeterioration and Biodegradation, Vol. 1* (Calcutta: Naya Prokash, 1993), 340.

²⁶ Jain, 340.

²⁷ Dr. A Elena Charola, personal communication.

²⁸ Winkler, 225.

²⁹ Caneva and Salvadori, 202.

³⁰ Jain, 340.

³¹ Caneva and Salvadori, 202.

³² Srinivasan, 107.

further biological growth as well as serving as a place for seeds to settle and grow.³³

Other Deterioration Mechanisms

Plants may also hide deterioration³⁴ such as open joints or eroded surfaces. Macroflora on a monument may also promote lower plant growth such as algae or lichens by creating a favorable microclimate to support microflora. Small plants growing close to the substrate create a more humid, hygroscopic environment with little direct sunlight which is favored by lower plant forms.³⁵ The microclimate of an area of vegetative growth is likely to be affected by levels of thermal radiation, retention of heat, and greater humidity.³⁶ Increased humidity results from retardation of water vapor removal and continual transpiration by living plants.³⁷ The water content is likely to increase with plants growing nearby, as is the amount of water stagnation.³⁸ In frequent wetting and drying cycles, the cells and mucilage layers may swell and shrink, causing damage through pressures.³⁹ Dense plant growth can also harbor harmful insects or rodents that

³³ Sujay Kumar Das, "Decaying Characteristic of Brick-built Monuments under Hot-Humid Climactic Conditions in West Bengal" in *Conservation of Cultural Property in India*, edited by N. Harinarayana (New Delhi: Indian Association for the Study of Conservation of Cultural Property, 1991), 71.

³⁴ Paul K. Goeldner, "Plant Life at Historic Properties" APT XVI No. 3&4 (1984): 67.

³⁵ Moug, 326.

³⁶ Fisher, 102.

³⁷ Fisher, 102.

³⁸ Garcia-Murillo, 658.

³⁹ H. A. Viles. and C. A. Moses, "SEM Based Studies on the Combined Effects of Salt and Biological Weathering on Calcareous Building Stones" in *Eighth International Congress on Deterioration and*

may cause building destruction.⁴⁰ If unchecked, a build-up of vegetation may result in fire threats during hot, dry seasons.⁴¹

Control of Plant Damage

There are many ways to control threatening plants. These range from mechanical, by man and by beast, to chemical. In prehistoric times man used his hands to remove weeds from his crops and by 1000 BC, with the adoption of animals to drag hoes, weed control became more effective.⁴² These methods are still used today for very small crops or in pre-industrial societies. Their practice has become far less common due to the time and energy expenditure that they require. With the advent of the mower, a new, less time consuming method was developed. Mowing can prevent seed formation and deplete food reserves.⁴³ However, mowing can only be safely done in open areas as the mower itself can cause chipping and cracking of masonry if used with too much force. Mulches, often used as crop fertilizers, may also be used to control weed

Conservation of Stone, Berlin, 30 Sept. - 4 Oct. 1996: Proceedings, edited by Josef Riederer (Berlin: S. N., 1996), 557.

⁴⁰ Fisher, 102.

⁴¹ G. Caneva and A. Altieri, "Biochemical Mechanisms of Stone Weathering Induced by Plant Growth" in *The Sixth International Congress of Stone Deterioration and Conservation, Proceedings, Torun, 12-14 September, 1988*, edited by J. Ciabach, (Torun: Nicholas Copernicus University Press Department, 1988), 33.

⁴² Floyd M. Ashton, *Weed Science: Principles and Practice*, Third Edition (New York: John Wiley and Sons, 1991), 4.

⁴³ Ashton, 40.

growth by reducing the amount of light that reaches potential weeds.⁴⁴ Controlled burning and flooding are two other possibilities for weed control in certain areas.⁴⁵ However, burning and flooding could cause further damage to historic masonry. Control through the use of certain crops or herbivores are other possibilities⁴⁶ but could cause more harm than good in the case of historic structures. This leads to the seemingly practical and efficient solution of applying chemical herbicides to unwanted plant growth.

⁴⁴ Ashton, 42.

⁴⁵ Ashton, 43-44.

⁴⁶ Ashton, 53-54.

Chapter Three: Herbicides

Every year thousands of weeds are eliminated by chemical methods. Herbicides are the most commonly used biocide in agriculture, in industry and in residential areas to keep crops, rights-of-way and lawns free from troublesome vegetation. One of the most commonly used herbicides in the conservation of historic sites is glyphosate. It is the active ingredient of the formulation Round-up[®], a commercial herbicide widely used in the United States and in many other countries. Because of its extensive use as a post-emergent, broad-spectrum method of weed control, Round-up[®] was chosen as the testing product in this thesis.¹

History of Herbicides²

In ancient times, salts were used to destroy unwanted plants³ because they drew water away from the root thus killing the plant. As early as 1675, vegetation growth was formally recognized as a problem.⁴ In the late 1800's, certain inorganic chemicals were found to have weed killing properties and were adopted into agricultural practices. In 1896, Bonnet, a French grapegrower,

¹ Extent of use determined through product research and personal communication with conservators and agencies such as National Park Service in the United States and English Heritage in the United Kingdom.

² The history and types of herbicides have been well documented in other sources such as L. J. Audus, Donald Elisha Harding Frear, Floyd M. Ashton and Alden S. Crafts to name a few. Therefore, details will not be covered here.

discovered that copper sulfate, killed charlock in cereal crops.⁵ Thus began the quest for effective herbicides. Other inorganic chemicals, such as sulfates, potassium salts and sulfuric acid, were also found to be destructive to weeds.⁶ Boron compounds, like borax, as well as chlorates were also studied as weed controls in the early 1900's.⁷

As the need for weed control increased with larger crops, organic compounds were developed for this purpose beginning in the 1930's. About the same time, the development of the greatest advance in weed control came with the development of hormone-type weed killers.⁸ The 1940's heralded the beginning of a modern herbicide industry.⁹ Intense research in the United States and in Europe resulted in hundreds of new chemicals for plant control.¹⁰ The production of herbicides increased dramatically between the years of 1950 and 1970. Since then, thousands of new chemicals have been developed to fight plant growth.

Herbicides cover a wide range of chemical groups and are identified by a trade name (Round-up®), a chemical name [N-(phosphonomethyl)glycine] and a common name (glyphosate). Herbicides are classified in several different

³ Office of Chemicals and Allied Products, *A Competitive Assessment of the U. S. Herbicide Industry* (Washington, D.C.: International Trade Administration, US Department of Commerce, 1985), 7.

⁴ L. J. Audus, *The Physiology and Biochemistry of Herbicides* (London: The Academic Press, 1964), 1.

⁵ Audus, 11.

⁶ Audus, 11.

⁷ Audus, 12.

⁸ Audus, 13.

⁹ Office of Chemicals and Allied Products, 1.

¹⁰ Office of Chemicals and Allied Products, 1.

ways. The first is alphabetically by their common or trade-name, such as Round-up® or Tordon®, and secondly, by their active ingredient such as glyphosate or amitrole. They may also be classified according to how they are used to produce maximum results such as the physiological characteristics of each herbicide which include halting growth processes, or prohibiting water from reaching the root system.¹¹

Herbicide Action

Many different parameters define how an herbicide works. Herbicide effectiveness is dependent upon soil type, climate, moisture, equipment and application.¹² An herbicide can be selective or non-selective. Selective herbicides will kill one specific type of plant and are less likely to affect those that grow contiguously. Non-selective herbicides destroy a larger spectrum of plants. Herbicides can be applied before planting, or before a plant emerges, called pre-emergent, or after a plant sprouts, known as post-emergent. They can be applied by broadcasting over a large area, in a narrow strip as a band, or in spot treatments, which are localized.

When discussing the action of herbicides two phrases must be clarified. The first is the “mode of action” of an herbicide which is defined in *Weed Control*

¹¹ Floyd M Ashton and Alden S Crafts, *Mode of Action of Herbicides* (New York: John Wiley and Sons, Inc., 1981), 7.

¹² William Olkowski, et al. *Common Sense Pest Control* (Newtown, CT: Tauton Press, 1991), 505.

by the National Academy of Science as “ the entire sequence of events from the introduction of the herbicide to the environment to the death of the plants”. The second concept is the “mechanism of action” which is the “primary biochemical or biophysical lesion leading to death.”¹³ Under “mode of action,” the absorption, translocation, and molecular fate of the herbicide, as well as biochemical responses, growth, and structure of the plant are considered.¹⁴

Once the herbicide is applied it must be absorbed by the plant and translocated (transported) to various parts; where it is molecularly altered creating a substance poisonous to the plant. The plant may absorb the herbicide through its leaves, its roots, the shoot, or the stem.¹⁵ The plant species and its age, environmental conditions, and herbicide characteristics will affect the results of the application.

Once the herbicide has been absorbed, it may attack one or more of the different vital processes of the plants. Certain chemical compounds act as a defoliant causing abscission of the leaves resulting in a bare stalk.¹⁶ Direct protoplasmic action and plasmolysis are also functions of the chemicals.¹⁷ Herbicides that affect growth through hormones can alter cell division, cell enlargement, tissue differentiation, and can cause cellular and tissue

¹³ Anon., *Principles of Plant and Animal Pest Control*, Vol. 2, *Weed Control* (Washington, D.C.: National Academy of Science, 1975), 471 as quoted in Aston and Crafts, 3.

¹⁴ Ashton and Crafts, 3.

¹⁵ Ashton, 79-82.

¹⁶ Donald Elisha Harding Frear, *Chemistry of Insecticides, Fungicides and Herbicides* (New York: Van Nostrand, 1948), 309.

deterioration. Some herbicides can also serve as a soil sterilant to prevent weed growth.¹⁸ All are intended to disrupt the growth process resulting in death.

Round-up® and Glyphosate

Glyphosate is a post-emergent, broad-spectrum, non-selective herbicide used in several herbicide formulations, the most well-known being Round-up®. In 1970, Dr. John E. Franz discovered the characteristics of glyphosate that made it an effective herbicide.¹⁹ Glyphosate is a weak organic acid with the empirical formula, C₃ H₈ NO₅ P and the structural formula as follows:

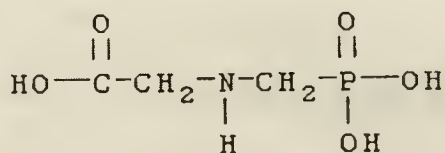


Figure 3: Structural formula of glyphosate

It is most commonly used in its isopropylamine salt form.²⁰ The characteristics of technical grade glyphosate found in Round-up® include low vapor pressure, high solubility in water, and a specific gravity of 1.704.²¹ It appears as an odorless

¹⁷ Frear, 310.

¹⁸ *Herbicide Manual for Noncropland Weeds* (Washington D.C.: Department of the Army, the Navy and the Air Force, 1970), 5.

¹⁹ *Glyphosate*, www.glyphosate.com/rndup/rdytech.html 28 July 1999.

²⁰ H. Mensink, and P Janssen, *Glyphosate*, Environmental Health Criteria 159 (Geneva, World Health Organization, 1994), 11.

²¹ Mensink, 11.

white crystalline powder. It is generally distributed as water-soluble concentrates and powders.²² Glyphosate eliminates plants via leaf chlorosis and formative effects²³ by inhibiting an enzyme necessary for synthesizing aromatic amino acids and thus for plant growth. It is applied directly to the leaves and stem and is translocated through the vascular system to all parts of the plant including the roots. Glyphosate can be used to eliminate herbaceous and non-herbaceous plants and in lower concentrations it may act as a growth regulator.²⁴ The pH of glyphosate has been measured to be acidic: between 2.5 to 4.99 in a 1% solution.²⁵ The chemical name of glyphosate is N-(phosphonomethyl) glycine.²⁶

Overall use of glyphosate is thought to be relatively safe to humans and most animals. Round-up®, in which glyphosate is found, has been given a “Caution” rating by the EPA, the lowest warning signal available. Even at high doses, only minor effects, such as microscopic alterations to the liver and kidneys and rare reproductive changes were seen in laboratory animals.²⁷ The LD₅₀ is 4873 mg/kg in rats. While toxicity to mammals is relatively low, some effects have been seen in other animal classes. Glyphosate has been found to be slightly toxic to some wild birds and some aquatic organisms.²⁸ After many

²² *Information Profiles*, Oregon State University, <http://ace.orst.edu/info/extonet/pips/glyphosa.htm> 28 July 1999.

²³ Ashton and Crafts, 17.

²⁴ Greenpeace, *Greenpeace Report- Not Ready for Roundup: Glyphosate Fact Sheet*. <http://www.greenpeace.org/~usa/reports/biodiversity/glyp.html> 28 July 1999.

²⁵ Mensink, 19 and MSDS for Round-up® from Monsanto.

²⁶ MSDS for Round-up® from Monsanto.

²⁷ <http://ace.orst.edu/info/extonet/pips/glyphosa.htm>.

²⁸ <http://ace.orst.edu/info/extonet/pips/glyphosa.htm>.

studies on the toxicity of glyphosate, it does not appear to pose any major health threat to humans or animals. Some skin and eye irritation may result with contact, and therefore appropriate safety cautions should be taken and the manufacturer's recommendations should be followed.

In 1974 glyphosate was introduced to the commercial market under the trade-name Round-up[®] by the Monsanto Corporation. Glyphosate accounts for 41% of the Round-up[®] formulation. In addition to water, the other ingredient in Round-up[®] is a surfactant blend of a phosphate ester neutralized polyethoxylated tallowamine.²⁹ The surfactant breaks down fatty and waxy plant tissues, reducing the surface tension on the leaf so the active ingredient can spread over it.³⁰ Like glyphosate, the surfactant in Round-up[®] is said to be relatively safe to man and the environment, resulting only in eye and skin irritation.³¹ The ethoxylated tallowamine makes up about 14.5% of concentrated Round-up[®].

Degradation of Glyphosate

The chemical glyphosate is broken down in several ways in the environment. Glyphosate is highly water soluble with an ionic character and will

²⁹ Monsanto Product Literature.

³⁰ Monsanto Product Literature.

³¹ Monsanto Product Literature.

therefore resist bioaccumulation.³² It is biodegradable and is broken down by microorganisms found in the soil. Bacteria can use the compound glyphosate as a sole source of phosphorous, carbon or nitrogen, nutrients used in their survival.³³ Biodegradation occurs more frequently in aerobic conditions.³⁴ Microorganisms degrade glyphosate in one of two ways. The first is through the formation of AMPA (aminomethylphosphonic acid, the main metabolite of glyphosate) and a carbon fragment, which might be glyoxylate (the salt of glyoxylic acid).³⁵ The second route is through sarcosine (also known as n-methyl-glycine) and orthophosphate after which sarcosine is broken down to glycine and a one carbon unit that may form carbon dioxide in formaldehyde.³⁶ If the same types of microorganisms are found in building materials, this use of glyphosate as a source of food may eventually promote regrowth. Some of these soil organisms are most certainly found in archaeological sites.

In addition to biodegradation by microorganisms, photodegradation may also occur. According to test data, sunlight decomposed very small amounts of the glyphosate in sterile aqueous buffers of pH 5, 7 and 9. The photodegradation of glyphosate was also examined in unpolluted and polluted water and in soil. Photodegradation was found to occur only in water and more

³² Mensink, 52

³³ Mensink, 45.

³⁴ Mensink, 44.

³⁵ Mensink, 48.

³⁶ Jacob, et, al, "Metabolism of Glyphosate in *Pseudomonas* sp. Strain LBr" *Applied Environmental Microbiology* 54(12): 2953-2958 as quoted in Mensink, 48.

slowly in polluted water, possibly due to reduced amounts of UV penetration and not in soil nor under artificial light.³⁷

Degradation through water and soil sorption are the most relevant to the use of glyphosate on buildings. Although the mechanism of soil sorption is only partially understood, it is known that glyphosate can readily bind to many soils and clay minerals.³⁸ As glyphosate degrades, the “phosphonic moiety adsorbs weakly to unoccupied phosphate binding sites and can be displaced by phosphate.”³⁹ Soil sorption of glyphosate is expected to occur with phosphate binding sites, the presence of iron and aluminum, and to an extent calcium, potassium and sodium, and with appropriate combinations of clay and organic matter.⁴⁰

As a water soluble compound, near a neutral pH, the formation of an insoluble precipitate can occur, when calcium is present.⁴¹ Insoluble complexes are also formed with magnesium, iron and copper.⁴² This is relevant for the use of Round-up® on masonry units and the potential binding with these ions from minerals in the stone to form disfiguring and potentially destructive insoluble complexes.

³⁷ Mensink, 43.

³⁸ P. Sprinkle, et al, “Adsorption, Mobility, and Microbial Degradation of Glyphosate in the Soil” *Weed Science* 23 (3) 1975: 229-234 as quoted in Mensink, 37.

³⁹ Mensink, 37.

⁴⁰ Mensink, 38.

⁴¹ Mensink, 34.

⁴² Mensink, 34.

Extensive study has also been performed on the fate of glyphosate in the environment. Glyphosate remains in the soil with an estimated half-life of 47 days in the laboratory and 1 to 174 days in the field.⁴³ It becomes tightly bonded to most soils, and therefore does not easily leach or run-off into the water table.⁴⁴ The most common way for glyphosate to disappear from the soil is through the action of microorganisms which breakdown the chemical. In bodies of water, the chemical is adsorbed to suspended organic and mineral particles, which are then broken down by microorganisms.⁴⁵ Its toxicity increases with higher water temperatures and a higher pH.

While the degradation of glyphosate is well-known, the degradation of the surfactant in Round-up® is not fully understood. By looking at structurally related compounds, it is likely that the ethoxylated tallowamine degrades fairly rapidly⁴⁶ and should have little residual effect on the environment but a large effect on the efficacy of the herbicide.

Potential Damage to Stone

There is no known study on the half-life of glyphosate in building materials. Because it is unknown how long the glyphosate remains in the material, several concerns might arise. It is unknown how residual glyphosate

⁴³ <http://ace.orst.edu/info/extonet/pips/glyphosa.htm>.

⁴⁴ <http://ace.orst.edu/info/extonet/pips/glyphosa.htm>.

⁴⁵ <http://ace.orst.edu/info/extonet/pips/glyphosa.htm>.

reacts to freeze/thaw cycles. If acidic glyphosate remains in the stone after application, it may be transported further into the stone with periods of wetness, causing further deterioration to the interior of the masonry via capillary action. Glyphosate may also provide nutrients for microorganisms living in the stone, which may restart the growth cycle. The effects of wet/dry cycles may increase salt formation from glyphosate, promoting salt damage.

A water and soluble salt combination is one of the most damaging stone mechanisms known. Soluble salts are dissolved and transported through the stone. As the water evaporates, they are redeposited elsewhere on and in the stone. They may appear within the stone in pores or on the surface as efflorescence. When deposited under the surface they crystallize as subflorescence and can cause exfoliation or disaggregation. When the stone becomes wet again, the salts redissolve and move to a new location causing further microcracking and pore expansion.

Salts may also intensify the effect of other decay mechanisms such as freeze/thaw damage.⁴⁶ The hygroscopic nature of some salts may increase the water content of stones. Soluble salts as well as insoluble salts may affect the ability of a stone to release water thus causing damage by clogging the pores. The amount of literature on salts and the damage they cause to stones is

⁴⁶Mensink, 52.

⁴⁷ Lubica Wessman, "Studies of Salt-Frost Attack on Natural Stone," in *Eight International Congress on Deterioration and Conservation of Stone, Proceedings, Berlin 30 September-4 October 1996*, edited by Josef Riederer (Berlin: S. N., 1996), 563-571.

significant and should be referred to for further information on this process of deterioration.

Legislation

As the use of herbicides for weed control became popular, government regulations were enacted to monitor the safe use of herbicides. The federal government first began regulating pesticides including herbicides, in 1910 with the Insecticides Act. This statute was intended to protect farmers from misbranded products.⁴⁸ As more products were developed, the Federal Insecticide, Rodenticide, and Fungicide Act (FIRFA), passed in 1947, broadened the government's control over pesticides. The government began looking at safety considerations concerning pesticides and required registration with the Department of Agriculture.⁴⁹ This jurisdiction was passed to the Environmental Protection Agency upon its establishment in 1970, adding another layer of concern: the environment.⁵⁰ In 1972, Congress passed the Federal Pesticide Control Act (FEPCA) which shifted the focus of federal law to controlling pesticides for reduction of unreasonable risks to man and to the environment.⁵¹

⁴⁸ Environmental Protection Agency. *Pesticides--The Federal Insecticide, Fungicide, and Rodenticide Act (FIRFA)*, <http://es.epa.gov/oeca/tped/firfatp.htm> 28 July, 1999.

⁴⁹ <http://es.epa.gov/oeca/tped/firfatp.htm>.

⁵⁰ <http://es.epa.gov/oeca/tped/firfatp.htm>.

⁵¹ <http://es.epa.gov/oeca/tped/firfatp.htm>.

Changes were made to accelerate the registration process in 1988 and again in 1996.⁵²

The basic statute, FIRFA, defines pesticides as "chemicals or other products used to kill, repel or control pests."⁵³ FIRFA regulates the sale and use of pesticides for an estimated 21,000 products in use.⁵⁴ In order to register any pesticide, extensive scientific data on pesticide toxicity and behavior in the environment must be submitted.⁵⁵ Under FIRFA, any pesticide must be registered with a label giving detailed instructions for safe use.⁵⁶ There are numerous others laws governing the use and sale of pesticides which may be referenced in *Laws and Institutional Mechanisms Controlling the Release of Pesticides into the Environment*, published by the Environmental Protection Agency.⁵⁷

National Park Service Policy

Because of the large number of historic sites under the management of the National Park Service their current policies were also considered in this brief synopsis. As a federal agency, the National Park Service is required to follow

⁵² Linda J. Schrienrow, *Federal Insecticide, Fungicide, and Rodenticide Act* (The Committee for the National Institute for the Environment) <http://www.cnie.org/nle/leg-81.htm> 28 July, 1999.

⁵³ <http://www.cnie.org/nle/leg-81.htm>.

⁵⁴ <http://www.cnie.org/nle/leg-81.htm>.

⁵⁵ <http://www.cnie.org/nle/leg-81.htm>.

⁵⁶ <http://es.epa.gov/oeca/tped/firfatp.htm>.

⁵⁷ Beatrice Holt Holmes, *Laws and Institutional Mechanisms Controlling the Release of Pesticides into the Environment* (Washington D. C: Environmental Protection Agency, 1972).

federal law. In addition, the National Park Service must also follow the laws of individual states and tribes, which regulate the use of certain herbicides.

National Park Service policy on herbicides and vegetation management can be found in two documents, NPS-77, *Natural Resources Management Guideline* and NPS-28, *Cultural Resources Management Guideline*. In regard to controlling vegetation around historic buildings, those managing vegetation “must keep the landscape in mind at all times.”⁵⁸ NPS-28 states that “the goal is to avoid unacceptable harm to both cultural resources and their environment.”⁵⁹ Vegetation management should be done only when necessary and in the case of cultural landscapes, “significant vegetation that causes damage to or threatens other resources is controlled rather than removed whenever feasible.”⁶⁰ Management must be aware of native and non-native species and whether or not elimination is appropriate to the site’s interpretation.⁶¹ In addition to compliance with FIRFA and state laws, any step to vegetation control must also comply with the National Environmental Protection Act (NEPA) and the Endangered Species Act. According to NPS-77, cultural techniques, including biological controls such as different vegetative species or grazing animals, to

⁵⁸ National Park Service, NPS-77, *Natural Resources Management Guideline* (Washington D. C. National Park Service, 1994), 2.

⁵⁹ National Park Service, NPS-28, *Cultural Resources Management Guideline* (Washington D. C. National Park Service, 1994), 49.

⁶⁰ NPS-28, 109.

⁶¹ NPS-77, 6-9.

control vegetation is preferable to chemical control of vegetation.⁶² However, introducing new plant species to control macroflora on an archaeological site or building would only exacerbate the problem of plant growth. NPS-77 also warns against increasing the concentration of any herbicide as it may burn off the leaves thereby reducing translocation and the effectiveness of the herbicide.⁶³ Knowledge of which plants are to be eliminated and the most ideal time to do so is also necessary before choosing an herbicide for the most effective eradication.⁶⁴

While the need for weed control is recognized by the National Park Service, there is no single recommended method. NPS-28 specifically states that “chemical or physical treatments that cause damage to historic materials are not used.”⁶⁵ According to Wayne Millington of the Integrated Pest Management Division, the preference to remove vegetation is by hand. Chemicals, such as Round-up®, should only be used as a last resort.⁶⁶

⁶² NPS-77, section 2.295.

⁶³ NPS-77, section 2.295.

⁶⁴ NPS-77, section 2.295.

⁶⁵ NPS-28, 107.

⁶⁶ Author’s Conversation with Wayne Millington IPM, February 26, 1999.

Chapter Four: Case Studies

Two National Park Service sites were selected as case studies based on the availability of representative masonry materials (natural stone and brick), the diverse environmental conditions, and available site information on past and present vegetation control. Moreover, both sites are interested in exploring better methods of vegetation control.

Fort Union National Monument Watrous, New Mexico

History

Fort Union National Monument is located near Watrous, in northeastern New Mexico. The average temperature at Fort Union ranges between 8° C in winter to 31° C in the summer with semi-arid conditions.¹ Rainfall averages at 46cm per year, enough to provide moisture for herbaceous plant growth. Fort Union is an important part of the history of the western United States, having served as a major military post and depot from its establishment in 1851 to its abandonment in the 1890's. Ruins of various adobe buildings including the officers' and soldiers' quarters, the commander's house, the guardhouse, the

¹ National Park Service, *Fort Union National Monument Home page*, <http://www.nps.gov/foun/index.htm>, 15 July, 1999.

quartermaster depot, the corrals and the hospital² are all that remain of a once thriving post. A majority of the remaining structures are low to the ground, while many of the features remain unexcavated. Most of the buildings were constructed of adobe with sandstone foundations, brick floors and some wooden elements.

As interest in the western frontier grew in the mid-eighteenth century, skirmishes with native peoples and the Spanish from Mexico spurred the need for a defensive fort in the territory which was later to become New Mexico.³ Colonel Edwin V. Sumner established the fort in 1851⁴ to serve as a major defensive post and a rest stop on the Santa Fe Trail which opened the West to new inhabitants and new trade opportunities. The military complex of the fort and depot went through several campaigns of demolition and rebuilding. After constructing a poor quality fort of pine logs, it was later rebuilt using earth in the shape of a star,⁵ a strategic plan used for many forts, in 1861. One year later, a third campaign of building took place. This time the fort was redesigned in the territorial-style with an extensive amount of supporting buildings and personnel.⁶ This third Fort Union became the largest fort in the American Southwest.⁷

² David Grant Noble, *Pueblos, Villages, Forts and Trails: A Guide to New Mexico's Past* (Albuquerque: University of New Mexico Press, 1994), 267.

³ Amy L. Freitag, "Cultural Landscape Study of Fort Union National Monument" (Master's thesis, University of Pennsylvania, 1994), 39.

⁴ Robert M. Utley, Introduction to *Fort Union and the Santa Fe Trail* (El Paso, Texas: Texas Western Press, 1989), xi.

⁵ Noble, 264.

⁶ Noble, 265.

⁷ <http://www.nps.gov/foun/index.htm>.

Fort Union developed into more of a settlement than a battle post having all the elements of a small community.⁸ With the coming of the railroads, the Santa Fe Trail rapidly became obsolete, and by 1891 Fort Union had lost its purpose.⁹ Because of their lack of use in later years, the fort's structures fell into disrepair and became shelters for squatters and like many abandoned sites, a source of building material for the local people.¹⁰ Shortly after the Union Land



Figure 4: Fort Union National Monument (reprinted from Robert M. Utley, *Fort Union and the Santa Fe Trail*)

and Grazing Company, the next owner, started demolishing structures, local citizens rallied to save the fort.¹¹ Through an uneasy contract, the National Park Service gained a portion of the land creating Fort Union National Monument in

⁸ F. Stanley, Introduction to *Fort Union*. (N.P.: World Press, 1953), x.

⁹ Freitag, 51.

¹⁰ Freitag, 52.

¹¹ Freitag, 52.

1959. The interpretive mandate for the site was recreation rather than restoration, necessitating ruins stabilization and continual maintenance.

Vegetation Growth and Herbicide Use

Because a site visit was not possible, a questionnaire was sent to gather information on vegetation growth and herbicide use at Fort Union National Monument. The site's Exhibit Specialist, Bob Hartzler kindly provided most of the following information.

Although vegetation at Fort Union has not appeared to cause any significant damage to the walls, the displacement and cracking of floor bricks are one result of extensive plant growth at the site. Vegetation at Fort Union consists primarily of grasses and herbaceous plants. Vegetation includes gramma grass (*Bouteloua oligostachya*), blue gramma, sideoats gramma, galleta, Switch grass (*Panicum virgatum*), Red-top (*Sporobolus airoides*), Blue-stem or Blue grass (*Agropyrum glaucum*), antelope grass (*Muhlenbergia gracillima*), Buffalo grass (*Buchloe* sp.), wild licorice (*Glycyrrhiza lepidota*), bottle brush, squirrletail, fringed and Bigelow sage, thistles, loco weed, vine mesquite, mullein, Indian paint brush, rabbitbrush, yucca, Palmer amaranth, pinyan, juniper and various wildflowers. Also present are invasive non-historic plants such as snake weed

(*Gutierrezia sarothrae*), sagebrush, oak, wolftail, threeawn and silver bluestem,¹² and the Fiesta daisy or annual sunflower (*helianthus annuus*) to name a few.¹³ Sandstone flagstone walks, sandstone foundations and remaining brick floors are in constant contact with potentially damaging vegetation. On average, vegetation covers approximately 30% of the building complex.

Vegetation is currently controlled mechanically by mowing and hand-pulling. However, certain areas, such as the foundations and brick floors are not regularly cleared of harmful plants for fear of causing further damage by mowing. The commercial herbicide Round-up® has been used in the past in an attempt to decrease the amount of vegetation, but due to concerns about potential masonry damage, use was discontinued a few years ago. Burning the weeds with a propane torch was also used for a few years on site and has also been abandoned.

San Juan Fortifications, National Historic Site San Juan, Puerto Rico

History

The Spanish fortifications of Puerto Rico are located in San Juan on the northern side of the island on a small islet. It is a coastal, tropical region where

¹² Sandra Schackel, "Historic Vegetation at Fort Union National Monument" (Santa Fe, New Mexico: National Park Service, October 1983) as quoted in Freitag, 23-24.

¹³ Gail D. Tierney and Phyllis Hughes, *Roadside Plants of New Mexico* (Santa Fe: Lightning Tree, 1983), 57 as quoted in Freitag, 24.

temperatures range between 23°C and 30°C yearly with 77% humidity on average, and an average of 125mm of rain per month. Rain showers or storms are a frequent occurrence, especially during the months of June through October (Hurricane Season). The San Juan Fortifications have been designated a National Historic Site and a World Heritage Site. The main components of the defense system include *Castillo de San Felipe del Morro*, or “El Morro,” *Castillo de San Cristobal* or “San Cristobal”, the city walls which encompass Old San Juan, and the fort *El Cañuelo*, located across the bay from El Morro. El Morro protected the western end of the city and the harbor, while San Cristobal served.



Figure 5: *Castillo de San Felipe del Morro, San Juan, Puerto Rico*

as a defense against land attacks from the east.¹⁴ The fortifications were originally built to defend the then small town of San Juan, a strategic stopping point for the shipment of Spanish goods and treasures from the New World back to Spain.

Construction on the fortifications began in the sixteenth century and continued intermittently for many years. Construction of El Morro began about 1540 and San Cristobal around 1634. Although construction of the city walls began in 1586, they were not completed until almost two hundred years later in 1783. Improvements on the fortification system were made from 1630 to 1650. With the exception of modern military additions, the plan of El Morro is quite similar to that of 1790.¹⁵

San Cristobal was substantially reconstructed in 1766 and 1785 with minor additions at various times throughout the nineteenth and twentieth centuries.¹⁶ While most of the fortification system remains intact, a few areas of the city walls, including the land gate, were demolished late in the nineteenth century and early in the twentieth century for city expansion. The majority of the fortifications visible today were built from 1765-1800.¹⁷ All structures were originally built of a native coarse-grained, calcareous sandstone, fired brick and

¹⁴ National Park Service, *San Juan National Historic Site*, <http://www.nps.gov/htdocs4/saju/parksig.html>, 15 July, 1999.

¹⁵ National Park Service, "The Fortifications of San Juan National Historic Site, Historic Structure Report" (Washington DC: National Park Service, Department of the Interior, 1991), 35.

¹⁶ National Park Service, HSR, 21.

various mortars with wooden and metal elements. Stucco was originally and subsequently applied to protect much of the masonry from the harsh maritime conditions. Many of these materials have been retained.

The small town of San Juan became a major battle ground soon after its establishment. The strength of the fortifications was first tested in 1595 when Sir Francis Drake attacked San Juan with the support of Queen Elizabeth I. A second English attack on the fort came just a few years later, a battle the Spanish nearly lost. In reaction to this close call, Spain refortified the city to improve its defenses.¹⁸ In 1625, Dutch merchants under General Boudewijn Hendricksz sought a stronghold in the New World and looked to San Juan to fulfill this purpose.¹⁹ This time the city itself was captured and burned spurring the Spanish to build a more worthy fort to protect their precious colony.²⁰ Again, new construction on the fortifications to improve their defensive qualities occurred between 1630 and 1650.²¹ While improvements to the fortifications continued, they retained a major defensive role in Spanish wars against other European countries. In 1765, and again in the 1790's the fortifications were

¹⁷ Albert Manucy and Ricardo Torres-Reyes, *The Forts of Old San Juan* (Riverside, Connecticut: The Chatham Press, Inc., 1973), 7.

¹⁸ National Park Service, *The Forts of Old San Juan* (Washington, D.C., n.d.), 39.

¹⁹ National Park Service, 39.

²⁰ National Park Service, 47.

²¹ National Park Service, HSR, 41.

strengthened creating what was known as a “Defense of the First Order”.²² By 1790, San Juan was considered one of the best fortified cities in the Caribbean.²³

As the revolutionary spirit spread from the American colonies to Europe and back to the Spanish colonies, all holdings, with the exception of Puerto Rico and Cuba, were lost.²⁴ As Spain lost its grip in the New World, the purpose of the fortifications in San Juan moved from the defense of the empire to the defense of the island. The last major battle seen by the San Juan Fortifications occurred during the Spanish-American War in 1898. In the peace talks, Spain ceded Puerto Rico to the United States. El Morro then became home to the United States Army as Fort Brooke and served as a strategic defense in World War I and II.²⁵ As the use of modern weapons increased, the need for fortifications decreased and the site was signed over to the National Park Service in 1961 creating the San Juan National Historic Site.

Vegetation Growth and Herbicide Use

Abundant biological growth occurs on the city walls and the forts as a result of high temperatures, high humidity, high rainfall and bright sunny days. Some of the stones are colored black because of large colonies of biological growth. In an analysis performed by R.J. Koestler, four known types of fungi were

²² National Park Service, 60.

²³ National Park Service, HSR, 41.

²⁴ National Park Service, 71.

found including *Fusarium oxysporium*, *Mycelia steritia* (Hyahine), *Mycelia steritia* (Dane) and *Cladosporium cladosporioides*.²⁶ The historic stones provide nutrients and a foothold for such microflora as well as for higher plant forms. Many types of tropical plants are found growing on the Fortification walls. Typical weeds found in the area are common plantain (*Plantago major*), common sowthistle (*Sonchus oleraceus*), Mexican pricklypoppy (*Argemone mexicana*), and fetid passionflower (*Passiflora foetida*). Other herbaceous growth may include balsam torchwood (*Amyris balsamifera*), (*Bucida tetraphylla*), gumbo limbo (*Bursera simaruba*), (*Clausia rosea*) and West Indian milkberry (*Chiococca alba*).²⁷ A full survey of plant species has not been undertaken. Most growth is found on areas that are not covered by stucco. On some wall sections, the growth is sparse while on others it completely covers the historic masonry wall. Extent of exposure and water content are the main reasons for this variation. The large cavities of the stone provide a place for seeds and spores to settle and germinate. Plants grow in the mortar joints, cracks or cavities in the stone and along the foundation walls.

In addition to the damage caused by roots, excess moisture can be seen running down the face of the wall beneath clumps of plants. Shade from plants

²⁵ National Park Service, 78.

²⁶ R. J. Koestler, Appendix E "Problems of Biological Growth on Stone Materials with Special Reference to the Fortifications of San Juan National Historic Site, Old San Juan, Puerto Rico" in National Park Service, "The Fortifications of San Juan National Historic Site, Historic Structure Report" (Washington DC: National Park Service, Department of the Interior, 1991), 6-7.

²⁷ Henri Alain Liogier, "Botany and Botanists in Puerto Rico" in *The Scientific Survey of Puerto Rico and the Virgin Islands, An Eighty-year Reassessment of the Islands' Natural History*, *Annals New York Academy of Sciences*, edited by Julio C. Figueroa Colon (New York: The New York Academy of Sciences, 1996), 50.

may retard evaporation further contributing to moisture problems¹ and lower forms of biological growth.

Information about past and current plant growth control practices was provided by Edwin Colon, Masonry Chief at the site. The current method of control is hand pulling; however, access to much of the wall is difficult. Because of the favorable climate, readily accessible nutrients, and size of the monument, maintenance crews are fighting a losing battle with nature. Just weeks after the backbreaking work of clearing the walls of growth had been completed, small plants began to sprout again. Herbicides have been used in the past, the most commonly used being Round-up[®]. However, due to concern that herbicides do cause damage to the masonry units, they are no longer used directly on the stone. Issues of vegetal growth have been a continuous problem for the Fortifications. In an earlier Historic Structure Report, numerous references were made to the removal of trees and vegetation, all marked as high priority.²

These monuments and many others of cultural and historic significance have fallen prey to the ever-present vegetation. Although many techniques have been tried, Round-up[®] has been proven to kill weeds. At both sites, however, its use was discontinued by the National Park Service for fear of future masonry

¹ National Park Service, HSR, 71.

² Edwin C. Bearss, *San Juan Fortifications, 1898-1958: San Juan National Historic Site, Puerto Rico*. (Denver, Colorado: Denver Service Center, 1984), 408-416.

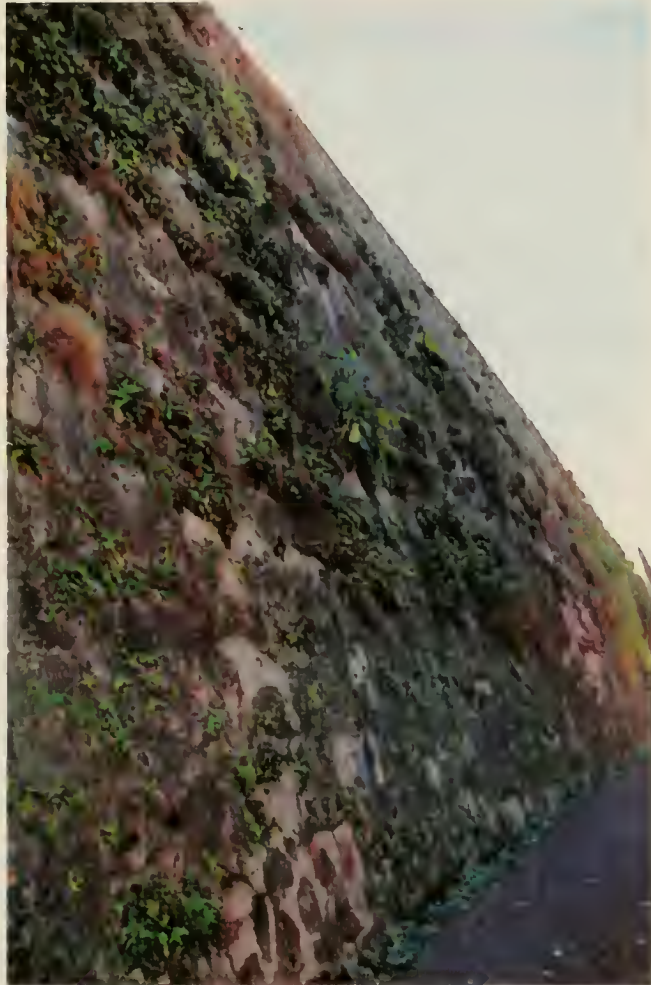


Figure 6: Extensive vegetation on San Juan Fortification Walls

deterioration. As a post-emergent herbicide, Round-up® also causes the plants to wither and dry up leaving unsightly plant remains. One must also consider the potential environmental effects to the surrounding ecosystems, which may come from herbicides. By evaluating the effects of this herbicide on the masonry, additional information can be brought into the decision-making process

Chapter Five: Testing Program

Methodology

The aim of this testing program was to evaluate the effects of the herbicide Round-up® and its surfactant have on selected masonry materials (brick and sandstone) from historic structures and archaeological sites. While recognizing that herbicides are applied as needed only a few times during a growing season, their cyclical use has suggested long-term exposure over time. The samples in this thesis were chosen for several reasons; first and foremost, to provide needed information on the potential dangers of herbicide use on historic masonry sites. The samples selected represent different masonry materials – low and high-fired brick, limestone, calcareous sandstone—in different states of weathering (exposed and unexposed). Considered were the physico-chemical differences of ceramic or fired materials versus natural stone materials and high quality versus low quality within each masonry type. The effect on acid soluble stone by the acidic herbicide was compared with the relatively acid insoluble bricks. The sites were chosen to examine tropical versus temperate environmental parameters, because plant growth is far more abundant in the tropics and more vegetation control is needed than in the temperate region. While this selection did cover a wide range of masonry components, it by no means covered all. There are many other types of stone

and architectural ceramics that may come into close contact with an herbicide that should be examined, including marble and granite.

This testing program was based on the concept of accelerated weathering. In this case, the concentration and exposure was increased to observe results which normally would occur over a longer period of time. It must also be remembered that limited parameters, that of the effect of the herbicide and its combination with tap water were examined. How that herbicide interacts with other conservation products, with other stones, in other climates and with other deterioration mechanisms was not examined in this study.

Pre-treatment

The masonry units chosen for experimentation with herbicides included calcareous sandstone from the San Juan Fortifications in Puerto Rico, Indiana limestone, historic brick from Fort Union National Monument, New Mexico, and new brick from Cava Building Suppliers in Philadelphia, Pennsylvania. Complete descriptions of these can be found in the section entitled Masonry Descriptions.

The Fort Union brick, the new brick and the Indiana limestone were cut into cubes, approximately 5 x 5 x 5cm³. The Fort Union brick was cut on a masonry saw with a carbide blade. The limestone was cut by the supplier (Cava Building Supplies) and the new brick, due to its hardness, was cut on an oil saw

using kerosene oil for easier cutting. The new brick was then immersed for several days in a solution of Dawn® detergent and water to remove the kerosene oils. Due to a limited amount of material, the San Juan sandstone was cut on a water saw into samples with similar weights but variable shapes. All samples were rinsed to remove loose material from the surface. The stones were dried in an oven at about 65° C to a constant weight.

First, the samples were examined by hand and their color, texture, shape and any unusual features were noted. Each sample was numbered and its sides determined (front, back, bottom etc.) for easier description of feature changes during testing. The number of cut sides on the sandstone and the number of sides having a fireskin on the bricks was also noted.

The next step consisted of measuring water absorption and porosity. The porosity of a material indicates the amount of pore space in a material. The more porous a material, the more water it can hold. The formula used to calculate porosity is

$$\% \text{ porosity} = v_p / v_a \times 100$$

where v_p is the volume of the pores calculated from the mass of the saturated sample minus the initial dry weight of the sample and v_a is the apparent volume. Apparent volume is the volume of a sample including the pores. Porosity is important because water is one of the most harmful substances to porous

building materials. It plays a role in most decay mechanisms including freeze/thaw, salt transportation, crystallization and hydration, and erosion of grains to name a few.

Qualitative microchemical tests were carried out to determine the salts present in each sample and the pH was measured to analyze the acidity or alkalinity of each. Microchemical tests are a simple, effective way to identify the type of salt that might be present as well as to obtain a semi-quantitative analysis of the salt (absence, trace, or large quantity). Salts are naturally found in many soils and stones and often play a major role in the deterioration of stone. By determining the specific salt type, diagnosis as to the origin of the salt as well as the intensity of deterioration caused by the salt can be assessed. Conductance of the stone leachings in a de-ionized water solution was also measured to assist in evaluation of the amount of salts found in the stones. A pH test determines the acidity or alkalinity of the stone which may help determine why the stone is deteriorating. A pH test is done by using either specially made pH indicator strips or by using a pH meter and evaluating the reading. The conductance and the pH were measured with an Omega pH/Conductivity Pocket Pal Meter.

Accelerated Weathering

The laboratory testing program, which was based on standards for testing salt resistance and weathering of masonry materials,¹ consisted of complete immersion for 24 hours and drying for another 24 hours. Seven cycles were run on the weathered stone and brick and ten cycles were run on the limestone and new brick to ensure results. The samples were placed bottom side down on glass beads or rods in plastic containers and covered with a lid to reduce evaporation.

The herbicide Round-up® was chosen for testing due to its widespread use reported in the conservation world, as well as at the selected sites. Three different solutions and a control were used. The control was simple tap water as Round-up® is likely to be mixed with a regular water source rather than laboratory de-ionized water. The second sample used was a mixture of tap water and ethoxylated tallow amine, the surfactant and the only other ingredient in Round-up®.² The ethoxylated tallow amine, when mixed according to the manufacturer's recommendations is about 2% and is used to reduce the surface tension on the leaf so that the active ingredient (glyphosate) can spread over the plant leaf.³ It also dissolves waxes on the plant.⁴ The third solution used was

¹ ASTM standard C-67 in *1998 Annual Book of ASTM Standards* (West Conshohocken, Pennsylvania: American Society for Testing and Materials, 1998).

² Round-up® Product Information from Monsanto Chemical Company.

³ Round-up® Product Information.

⁴ Round-up® Product Information.

concentrated Round-up® herbicide mixed with tap water to the manufacturer's recommendations making a solution of 17% Round-up® in water. The fourth solution was Round-up® mixed with tap water to a concentration double the manufacturer's recommendations to increase the speed and intensity of reaction (34% solution of Round-up® to water). While Round-up® has been proven



Figure 8: Immersion of samples

to be effective after only one or two applications in a given season, applicators may feel that a double dose will increase its speed or effectiveness.

To simulate more realistic conditions, the stones were air-dried outside the Architectural Conservation Laboratory at the University of Pennsylvania. The

temperature ranged from 18°C to 32°C and the average relative humidity in June was about 64%. A protective chamber using a plastic drop cloth was designed to protect the samples from inclement weather.



Figure 9: Samples drying outside

Evaluation of Deterioration

After the cycling was completed, more measurements were taken to compare with the pre-treatment data. The samples were again dried in the oven at a temperature of about 65°C to remove residual moisture and to achieve constant weight. Microchemical analysis, pH and conductance from each solution were measured. Residue from the stone was filtered to evaluate the

amount of material lost in the solutions. Residue that was stuck to the glass beads was removed by ultrasonic cleaning with a Fisher Scientific Ultrasonic Cleaner. Some samples were prepared for thin-section examination while the others were used for comparative testing.

Additional tests included hygroscopicity measurements to determine if the use of an herbicide would increase the attraction between water vapor and the stone. Hygroscopicity is the ability of a stone to absorb water vapor from the surrounding air. The porosity and water absorption capacity can affect the ability of the stone to absorb water vapor. The presence of soluble salts can also affect the hygroscopicity. After reaching a constant weight, the stones were placed on



Figure 10: Stones in 100% Relative Humidity Chamber

racks in a plastic tub with 3.5cm of water in the bottom to create an environment of 100% relative humidity. The lid of the tub was covered with paper towels to absorb condensation and to prevent it from falling onto the samples. The tub was then sealed with duct tape. The samples were weighed weekly to measure the water adsorbed.

The samples were also examined for any change in color. A Hunter Labscan II Colorimeter was used to determine whether the sample turned darker or lighter or changed in hue.

In addition to the physical and chemical tests described above, thin-sections were made to assist in stone characterization and alteration. Selected thin-sections were made to evaluate potential changes to the stone's mineralogy. In addition to thin-sections before treatment, one sample from the solution of tap water, one from the surfactant solution and one from the 34% solution of Round-up[®] was made for the Fort Union brick, the San Juan sandstone and the Indiana limestone. Due to a lack of visible results on the new brick, only a pre-treatment thin-section and a thin-section from the 34% solution of Round-up[®] in tap water was made. Thin-sections consisted of normal mounting impregnation on one half and impregnation with Polysupra Kregersol Blue pigment on the other half to facilitate the examination of salts⁵.

⁵ Thin-sections were cut by Spectrum Petrographics, Inc. in Winston, Oregon.

Chapter Six: Test Results

After only two cycles, changes were apparent. The samples were altered both physically and chemically. By identifying and analyzing these changes, the effects of herbicides on similar masonry materials may be evaluated and predicted. More extensive analysis techniques, such as Scanning Electron Microscopy, Energy Dispersive X-ray Spectroscopy and Fourier Transform Infrared Spectroscopy, are available to measure these changes and might be used for further analysis in the future.

Visual Analysis -- Pre-treatment

Twelve pieces of each sample type were evenly divided among the four solutions. For purposes of understanding the results, Samples 1, 2 and 3 of each masonry grouping were placed in the 34% solution, samples A, B and C, were placed in the surfactant solution, a, b, and c went into the 17% solution and R, I, and T were placed in the tap water control. Before immersion, the samples were visually examined, as described in next section, as well as characterized petrographically, in the petrography section.

Masonry Descriptions

San Juan Sandstone

The first sample is an inhomogeneous, calcareous sandstone, a clastic sedimentary rock, from the Fortifications in San Juan, Puerto Rico. The sandstone is a coarse-grained material with a calcite cement. It is a buff colored stone with hues ranging from pink to orange. On site, the stone sometimes appears black due to microbiological growth. Some green algae growth is also visible. The porous stone is friable and grains are easily separated when scraped. Samples were collected on site from displaced masonry units.

Indiana Limestone

The second sample chosen for testing is commercial "Indiana limestone." The freshly cut samples were obtained from CAVA Building Supply in Philadelphia, Pennsylvania. The stone is medium gray with different sedimentary layers distinguished by a slightly darker gray. The limestone is a homogenous, fine-grained, smooth, massive, stone. It is commonly used in twentieth century buildings.

Fort Union Brick

The third sample is a soft, machine-made, molded brick from Fort Union National Monument in New Mexico. The brick has a deep orange-red to pale orange-red color. Few large aggregate grains are visible. There are several vughs throughout the bricks. Biological growths, such as lichen and algae, were evident on the samples. The edges of the bricks are worn and chipped from use. The average original size of the machine-made bricks is approximately 20 x 10 x 6.5cm. They were originally used in floors and hearths.

New Brick

The fourth sample is a modern extruded brick. It has a deep red color, from large amounts of iron, with various types of aggregate protruding from the surface, resulting in a roughened fireskin. The brick is very dense and solid. Few vughs are visible.

Visual Changes

The most obvious effects of the herbicide on the stone could clearly be seen with the naked eye. After two cycles of immersion and drying, surface deterioration was visible. Salt efflorescence and surface loss were the most obvious mechanisms of deterioration at work. All the solutions produced varying

degrees of deterioration on most of the samples. The tap water control produced few strong results. Little deterioration other than slight material loss was visible on the Fort Union brick, Indiana limestone and new brick. There was greater loss on the San Juan sandstone, most visible on the sides that had been cut. In the solution of surfactant and tap water, once again, little deterioration was visible. All the stones remained relatively intact with the exception of the San Juan sandstone, which again had minor loss on the cut sides.

After two cycles, both herbicide solutions produced visible deterioration on all samples except for the new brick. The San Juan sandstone lost surface material and small salt pustules began to form. The solutions produced disaggregation, the formation of small salt crystals, and visible pitting on the cut surfaces. Deterioration of the limestone consisted of salt formation on the surface and pitting which created a rough surface. On the Fort Union brick, efflorescence formed, primarily on the fireskin. No other deterioration mechanism was visible to the naked eye. Surface loss and salt formation continued for the remaining cycles. After the third cycle, a color change was evident on the sandstone and limestone. By the fourth cycle, no new changes occurred on any samples except for the sandstone in the 34% solution of Round-up®. The surface grains on the natural sides lost definition, and the cement changed, producing a glazed appearance. All deterioration mechanisms intensified as the cycles increased. At the end of the cycling, seven cycles for

the weathered samples and ten for the unweathered samples, the stones and bricks were carefully examined for any changes.

San Juan Sandstone

The San Juan sandstone had less visible evidence of salt formation in comparison with the other samples. Fewer salt pustules were found on the San Juan samples than on the Fort Union brick and a salt haze covered portions of the cut sides. The cut sides showed considerable pitting and disaggregation on all the samples, but was most conspicuous on the samples immersed in the herbicide. Several of the samples also lost the grain definition on the natural sides. These sides took on a glazed appearance. There was also a clear visible color change in the samples that were immersed in herbicide.

Indiana Limestone

The Indiana limestone also exhibited extensive visual effects from the herbicides. Salt growth appeared on the samples immersed in the 34% solution of the herbicide, and to a lesser extent on those immersed in 17% solution. Small pustules and small crystals appeared over all sides of these samples. The surface of the limestone, once smooth, was now covered in small pits resulting in a rough surface. There was also a distinct color change in the samples immersed in 34% solution from gray to a brownish gray. Slight surface loss

occurred with the tap water control and the surfactant solution, but neither of these produced the intense roughening of the surface.

Fort Union Brick

The Fort Union brick samples immersed in the herbicide solution were covered in efflorescence. Approximately 90% of the fireskin and approximately 20% of the cut sides of the bricks were covered with a fine, white powder. There was slight surface loss. The edges of the samples were rougher and the aggregate was more pronounced than before treatment under low magnification. The bricks also seemed softer and more friable than before testing. There was no obvious color change.

New Brick

There was little visual change in the new brick. No visible salt crystals formed. A salt haze appeared over portions of the bricks immersed in the herbicide solutions. Calcium carbonate particles in the brick powdered after immersion in the herbicide. The surface on the fireskin felt slightly smoother, a result of minor surface loss. There was no visible color change.



Figure 10: San Juan sandstone from left to right: immersed in tap water (I), surfactant solution (A), 17% herbicide solution (a) and 34% herbicide solution (2)

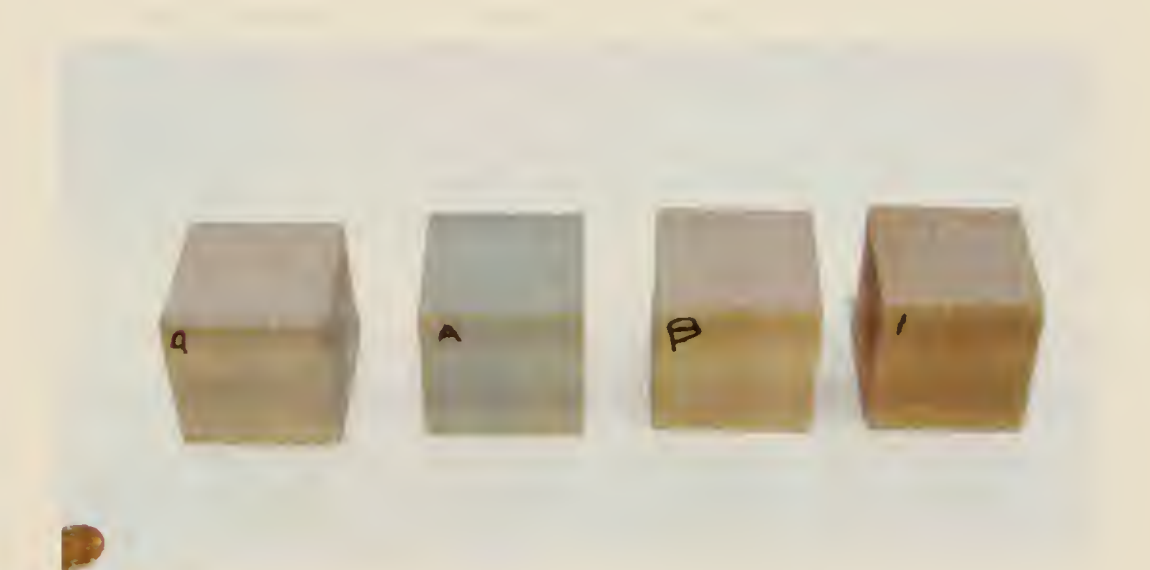


Figure 11: Indiana limestone from left to right: immersed in tap water (I), surfactant solution (A), 17% herbicide solution (b) and 34% herbicide solution (1)



Figure 12: Fort Union brick from left to right: immersed in tap water (I), surfactant solution (A), 17% herbicide solution (a) and 34% herbicide solution (2)



Figure 13: New brick from left to right: immersed in 34% herbicide solution (1), 17% herbicide solution (a), surfactant solution (A), and tap water (R)

Petrography

Selected samples were cut for thin-section analysis. One thin-section of each type of sample was made before treatment to characterize them and for comparison to the post-treatment samples. Thin-sections from the tap water control, the surfactant solution and the 34% herbicide solution were made for the sandstone, the limestone and the historic brick. Due to a lack of visual evidence on the new brick, only a thin-section from a sample in the 34% herbicide solution was made. All thin-sections were made with a bedding medium of Epotek 301 from Epoxy Technology and polished to a thickness of 30 μm , which permits light to travel through the sample. Half of the post-treatment thin-sections were pigmented with Polysupra Kregersol Blue from Special-t Coatings for easier detection of salts. Photographs were taken using Zeiss Axiophot MC100 polarizing light microscope by Dr. Gomaa I. Omar of the Department of Earth and Environmental Sciences at the University of Pennsylvania. The others were taken by the author on a Nikon Optiphot-pol polarizing Microscope. Photographs may be found following this chapter.

San Juan Sandstone

The San Juan calcareous sandstone contains a large number of allochemical components or allochems “which are organized aggregates of

carbonate sediment which have formed within the basin of deposition.”¹ The remaining aggregate is primarily quartz. Quartz grains are distinguishable under polarized light by their gray shades and a 90° extinction angle. The aggregate is cemented by calcium carbonate. The allochems or fossils are generally medium-sized and rounded while the quartz grains are small to medium and angular. The allochems found in the San Juan sandstone are classified as ooids, or “spherical to elipsoid bodies with a nucleus and radial or concentric structure,”² peloids “which are grains composed of micrite and lacking any recognizable internal structure,”³ and bioclasts (skeletal particles) such as coral and algae. The allochems and quartz grains consist of about 60% of the stone components. The pores are classified as channels and vugs and range in size from very small to very large. The packing of this stone is described as floating, meaning that few grains that are tangent to one another.

Indiana Limestone

The Indiana limestone also includes a large number of allochems with the remaining aggregate constituted primarily of quartz. The allochems have rounded edges and are both spherical and elongated. The Indiana limestone contains peloids and bioclasts including foraminifera and echinoderms as well as

¹ A.E. Adams, W.S. MacKenzie and C. Guilford. *Atlas of Sedimentary Rocks under the Microscope*. New York: Halsted Press, a division of John Wiley and Sons, 1984, 34.

² Peter Scholle, *A Color Illustrated Guide to Carbonate Rocks Constituents, Textures, Cements, and Porosities*, (Tulsa, Oklahoma: the American Association of Petroleum geologists, 1978), vii.

several species of micrite-walled forams (endothyraeids). The quartz grains are more angular and squared. The pores are very sparse, very small and rounded. The grains, which comprise about 85% of the structure of the stone, are cemented by calcite. The packing of this stone is described as "tangent" meaning that edges of the aggregate grains are in contact.

Fort Union Brick

The grains of the Fort Union brick are also primarily quartz and range from large to small, angular to rounded. The quartz grains are well distributed throughout the clay matrix and account for about 30% of the sample. There is a greater number of pores throughout the matrix of this brick. There is no direct connection between the grains and pores. The pores are variable shapes and sizes.

New Brick

The new brick consists primarily of clay and quartz grains. The majority of the grains are fairly large and angular surrounded by a fine particle clay matrix. The aggregate grains account for about 20% of the sample. Most of the pores are angular and tangential to the large grains in the brick. Some smaller pores

³ Adams, 36.

can be seen throughout the matrix along with small minerals which are probably quartz.

Post-treatment

San Juan sandstone

After seven cycles of immersion and drying, the San Juan sandstone exhibited extensive deterioration which was visible in the thin-sections. In each thin-section the pore space increased by the enlargement of pores and the creation of new ones. Because the sample is friable, this effect may be partially attributed to wetting and drying. An even greater effect was seen in the thin-sections of the samples immersed in herbicide solution. The acidity of the solutions caused the loss of large fragments of material resulting in larger pores. There was also some salt deposition on the pore surfaces.

Indiana limestone

In petrographic examination, the limestone was also noticeably affected by the different solutions. All samples, even those immersed in tap water, showed an increase in the amount of visible pores in the matrix. Small amounts of material were lost while soaking in tap water and the surfactant solution. Larger amounts of lost material were seen in the samples immersed in the 34% solution, which can, once again be attributed to the acidic glyphosate. When

comparing the two surfaces from the limestone sample immersed in the tap water and the limestone sample immersed in the 34% solution of herbicide, it is clear that there was significant surface loss.

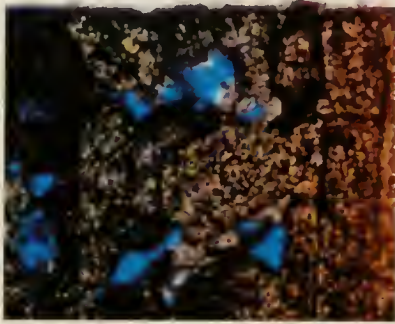


Figure 14: Surface of Indiana Limestone immersed water

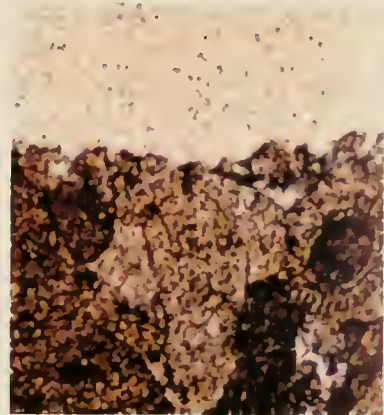


Figure 15: Surface of Indiana Limestone immersed in 34% herbicide solution

Fort Union brick

As with the other samples, the most noticeable change in the Fort Union brick was an increase in pores. The pores have increased slightly in size and amount. There is also an increase in the number of capillaries. Because these bricks appear to be well-fired, little visible deterioration was apparent.

New brick

Even after ten cycles of immersion in a 34% solution of herbicide, there was no visible effect in the thin sections of the new brick. There was no visible

salt deposition, nor large increase in pore space. The pores continued to appear in close proximity to the grains.

An increase in the pore space of the stone and the deposition of salts was expected based on literature about the product's acidity and was clearly seen in the thin sections. However, mineral etching resulting from the low pH of the solution though expected, was not evident.

Color Change

On several samples a distinct color change was apparent. The sandstone in the 34% solution of Round-up changed from a buff color to an orangish-yellow. The limestone changed from a medium gray to a brownish, dark gray. As indicated by the data below from the Hunter Labscan II Colorimeter⁴ a significant color change ensued from the herbicide. This type of change has been recorded in previous tests of glyphosate.⁵

Each measurement recorded by the colorimeter reads a different component of the color that humans see with their eyes. The "L" measures the lightness or darkness, "a" measures the amount of red or green, and "b

⁴ Data collected by Joshua Freedland of ELF-AUTOCHEM NA at their King of Prussia Research Laboratory in Pennsylvania.

⁵ Nugari, Pallechi and Pinna.

measures the amount of yellow or blue. The formula to determine color change is

$$\Delta E = [(L_c - L_x) + (a_c - a_x) + (b_c - b_x)]^{1/2}$$

Sample	L	a	b	ΔE
SJU 1	69.86	8.88	16.78	14.215
SJU B	73.11	6.42	19.74	2.813
SJU a	73.59	5.83	21.51	5.407
SJU T	75.94	4.67	16.78	
FtU 2	52.00	16.38	22.29	3.517
FtU C	49.56	16.46	22.97	5.771
FtU a	53.58	15.61	21.34	2.637
FtU T	54.61	14.30	12.20	
LS 3	55.12	2.82	13.12	14.111
LS B	71.63	0.78	6.02	3.990
LS c	63.58	1.84	10.46	5.267
LS I	68.12	1.32	7.84	
NB 2	39.17	15.62	15.06	3.163
NB C	40.39	15.99	15.32	1.458
NB c	41.66	15.51	14.77	2.637
NB R	42.33	15.60	15.19	

Figure 16: Data from Hunter Labscan II Colorimeter

The samples immersed in the tap water were used as the control for the color change measurements and are highlighted with gray on the chart. Minor color changes were detected in all the solutions with major color changes occurring in the 34% solution. A number recorded at 5 or above in the ΔE column indicates a clearly visible color change. Sample C from the Fort Union brick appears to be a color change but is not because a darker colored brick was originally used in the surfactant solution. The color changes seen are likely to be a function of the

low pH of glyphosate as evidenced by the author in an acid solubility test on similar samples.

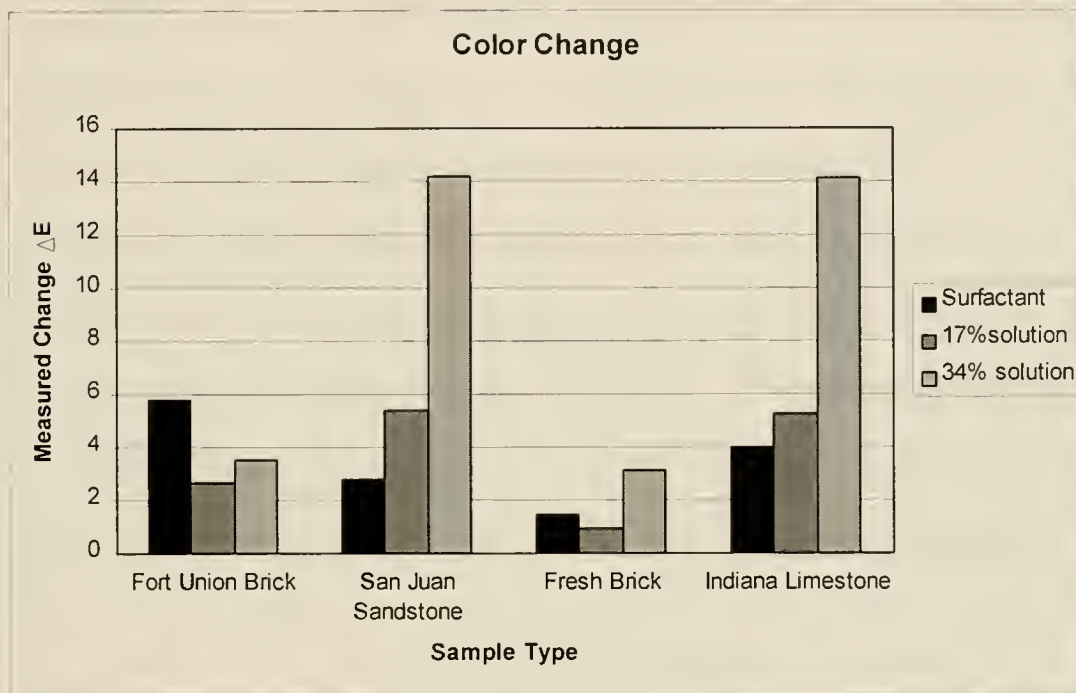


Figure 17: Color change in samples

Weight change

Overall, there was some weight change in all the samples. The samples were weighed before and after treatment. Residual material remained in the solution containers from the samples and from the formation of the insoluble calcium complex that is characteristic of glyphosate. By subtracting the weight (post-treatment) from the weight (pre-treatment) and then subtracting the weight of the residue, a total weight change was determined.

Both the San Juan sandstone and the Indiana limestone showed loss in all solutions. This is due to the friable nature of the natural stone and its susceptibility to acid. The sandstone, a poorer quality stone, had the most significant weight loss. The Fort Union brick gained weight in the two herbicide solutions. This may be attributable to the excessive salt growth covering the sample. The weight of this brick may have been less affected by the herbicide because it is fired at high temperatures sintering the clay minerals with a stronger bond than that found in the natural stone. The herbicide had little effect on the fresh brick. All weight change of the new brick was calculated to less than a gram, a very insignificant amount. However, the fresh brick did gain a

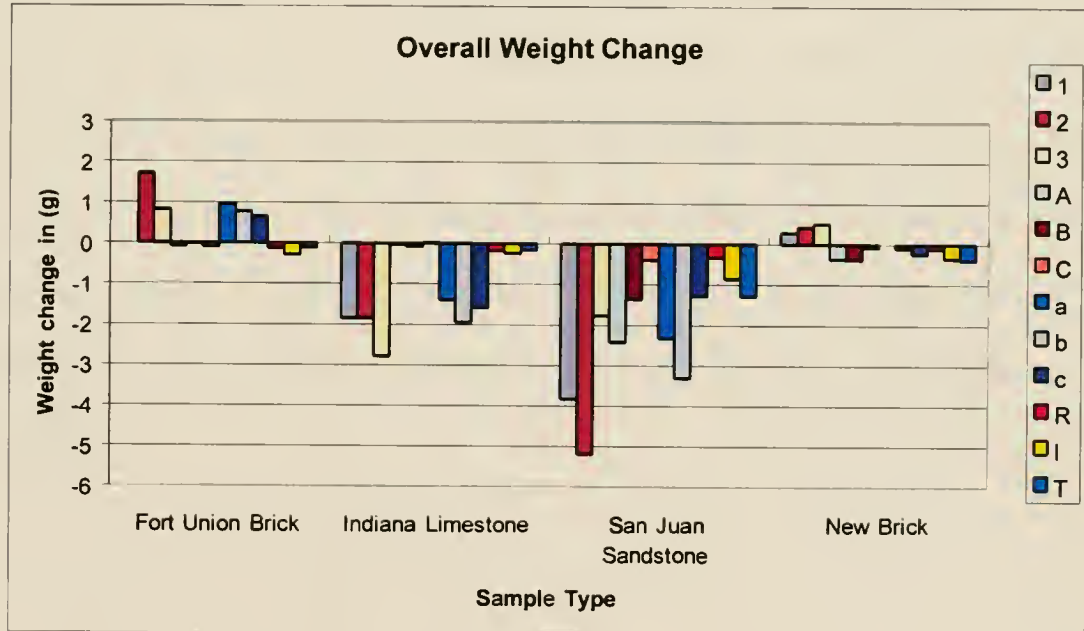


Figure 18: Graph illustrating overall weight change, note the weight loss of the sandstone and the limestone

amount of weight in the 34% solution which may be attributable to salt deposits. Detailed measurements may be found in Appendix C.

Porosity

In all samples, changes in porosity did occur. The porosity in the San Juan sandstone increased. This was expected considering the amount of material loss evident in the change in weight and in the thin-sections. Most of the limestone and Fort Union samples decreased slightly in porosity. This may be attributable to experimental error rather than any action of the herbicide, as it did not occur selectively. The new brick showed non-selective increases and decreases and can once again be attributable to experimental error. The experimental error may include too much or too little drying of each stone as well as weather changes. The porosity test was largely inconclusive and more advanced methods such as mercury porosimetry or computerized pore measurements should be used to determine any changes. Data may be found in Appendix C.

Salt Content

The amount of salts was measured in the sample leachings remaining in the test solutions. The samples had a small amount of salts present before testing. These were not removed because when using an herbicide in the field, one is unlikely to be dealing with salt-free masonry. On average, the 34% solution had a much greater conductance than that of the other solutions indicating that there has been an increase in ions through the herbicide and the tap water. The conductance found in the 17% solution was approximately double that of the conductance of the tap water solutions.

The samples had slight traces of various salts before undergoing the immersion process. After immersion, it was expected to find the same salts in the herbicide solutions as in the tap water solutions. However, traces of sulfates, chlorides, nitrites, and nitrates were found in the tap water leachings, but not in the 34% solution of the herbicide. This solution had sulfates, carbonates, chlorides and phosphates present. Very slight traces of nitrates and nitrites were found in the 17% solution in addition to the sulfates, carbonates, chlorides and phosphates. The surfactant solution had only nitrites found in addition to the others in the tap water and no phosphates.

The salt efflorescence found on the surface of the samples was insoluble, indicating that a chemical reaction took place to form insoluble material. This is

probably the calcium-phosphate salt that is formed by glyphosate in water as described in the section on degradation of glyphosate. A microchemical test for both calcium and phosphate confirmed their presence. Detailed results may be found in Appendix C.

pH levels

The pH levels of the sample leachings were tested before immersion and were measures slightly basic, all between 7.5 and 8 on the pH meter. Th pH levels of the initial solutions was also tested before immersion. The tap water had a pH of 7.1, the 17% solution a pH of 5.5 and the 34% solution a pH of 4.5. After immersion, the solutions were tested again and the pH had changed. The 34% herbicide had the lowest pH ranging from about 4.5 to 6.5. This change may be attributed to the glyphosate which is acidic. The other solutions measured higher. The increased pH may be attributed to the tap water which is fairly neutral. Data may be found in Appendix C.

Hygroscopicity

The stones immersed in the 34% herbicide solution were only slightly more hygroscopic than the tap water solutions. The herbicides immersed in the surfactant showed the least amount of water gain and the 17% solution samples were only slightly more hygroscopic than the surfactant samples. The most hygroscopic samples were the Fort Union bricks immersed in the 34% solution.

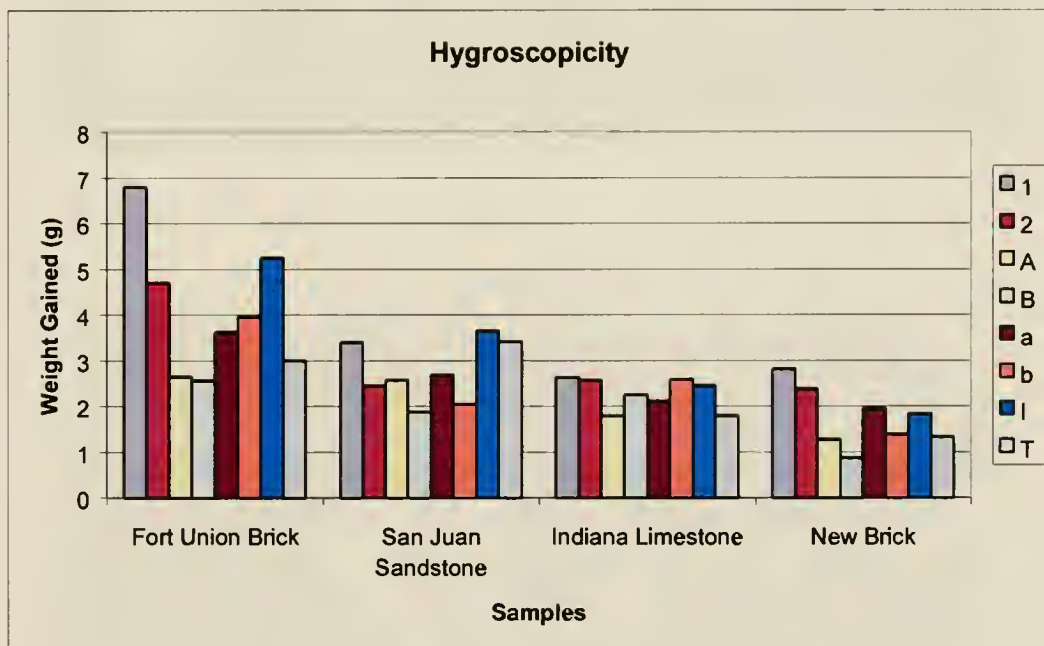


Figure 19: Chart illustrating hygroscopicity measurements of each sample tested

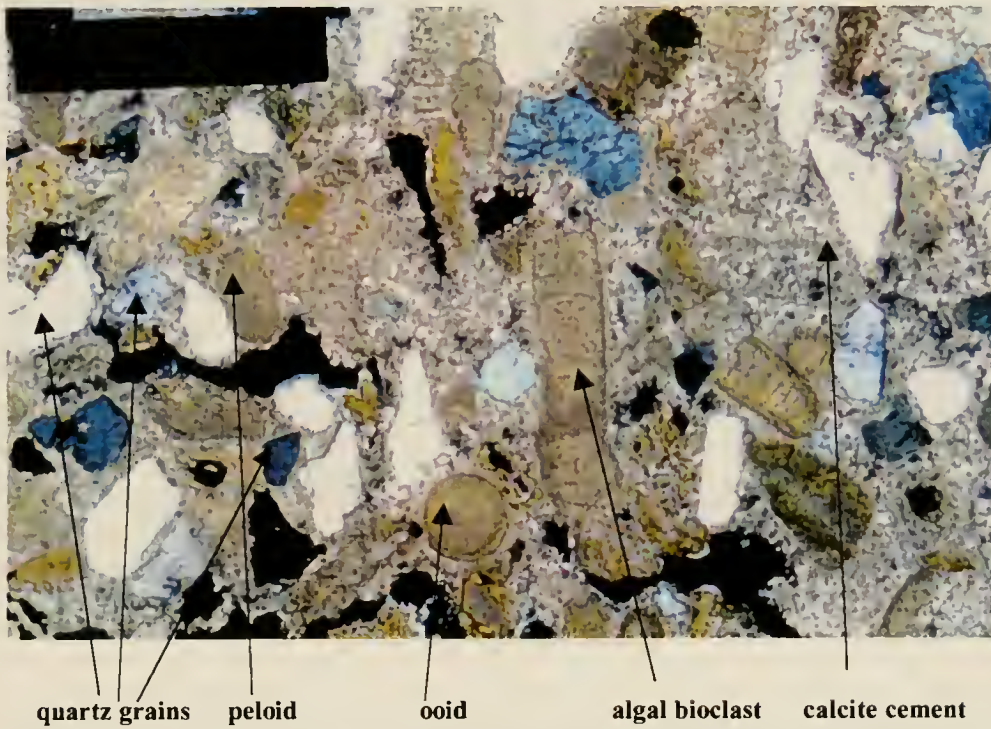
Petrographic Micrographs

Figure 20: San Juan sandstone before treatment, 25X

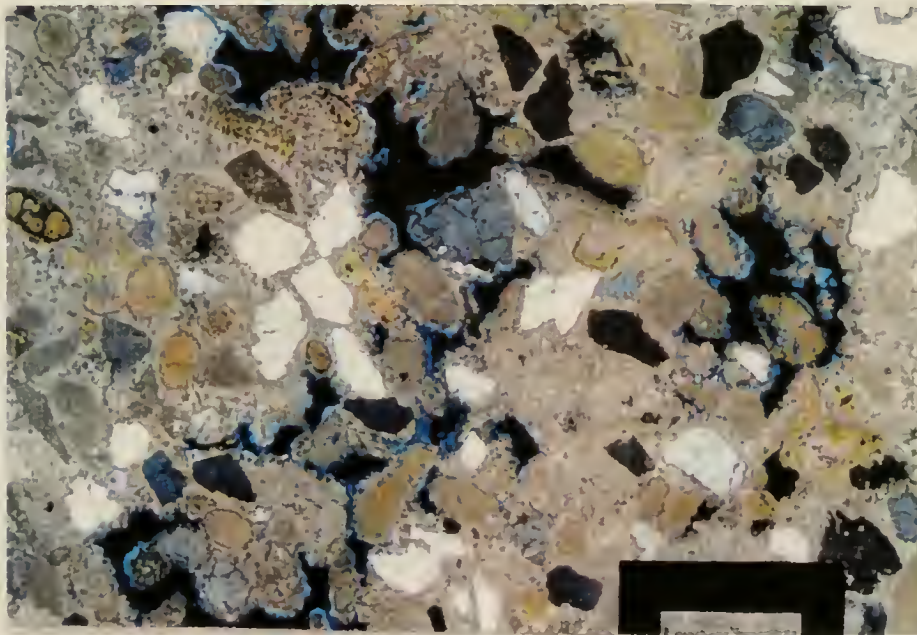


Figure 21: San Juan sandstone in tap water, 25x, Note increase in pore space and blue tinted salts

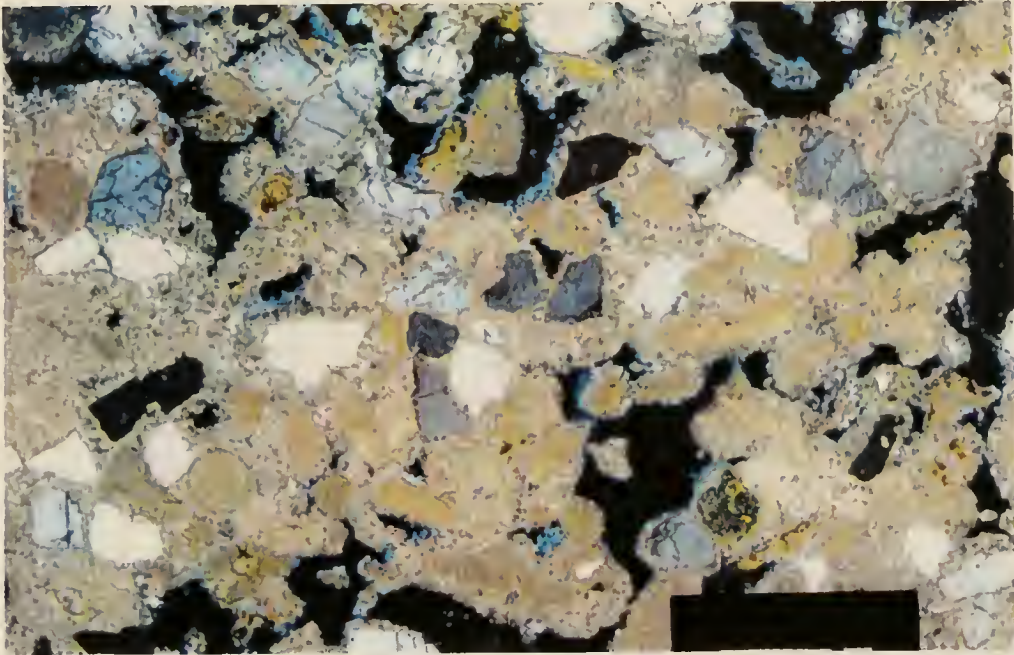


Figure 23: San Juan sandstone from surfactant solution, 25X, Note results similar to tap water solution

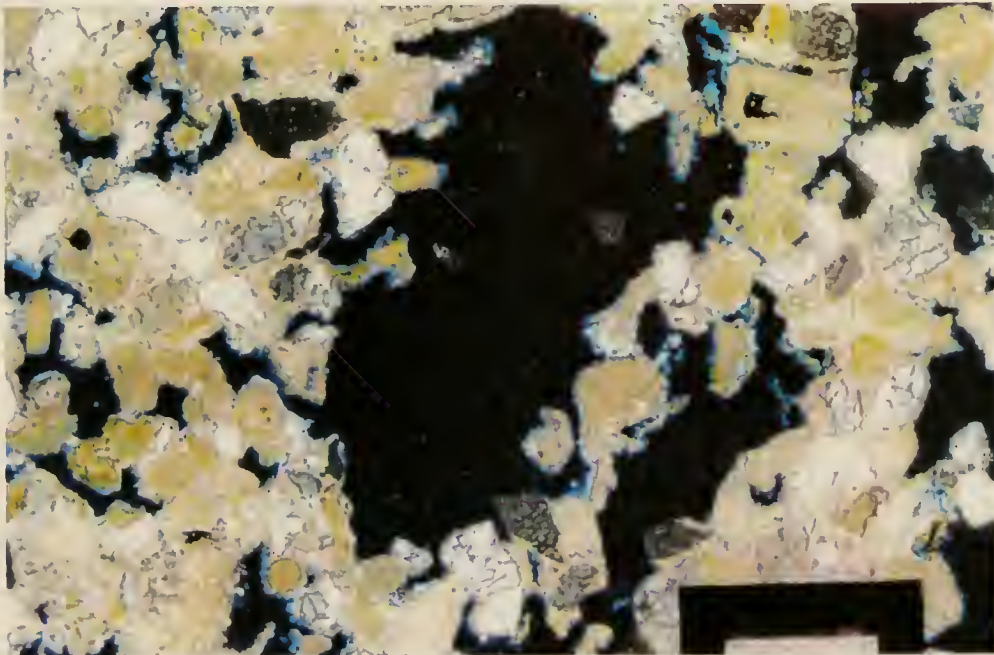


Figure 24: San Juan sandstone immersed in 34% Round-up® solution, 25X, Note larger pores, loss of calcite cement and salt deposits



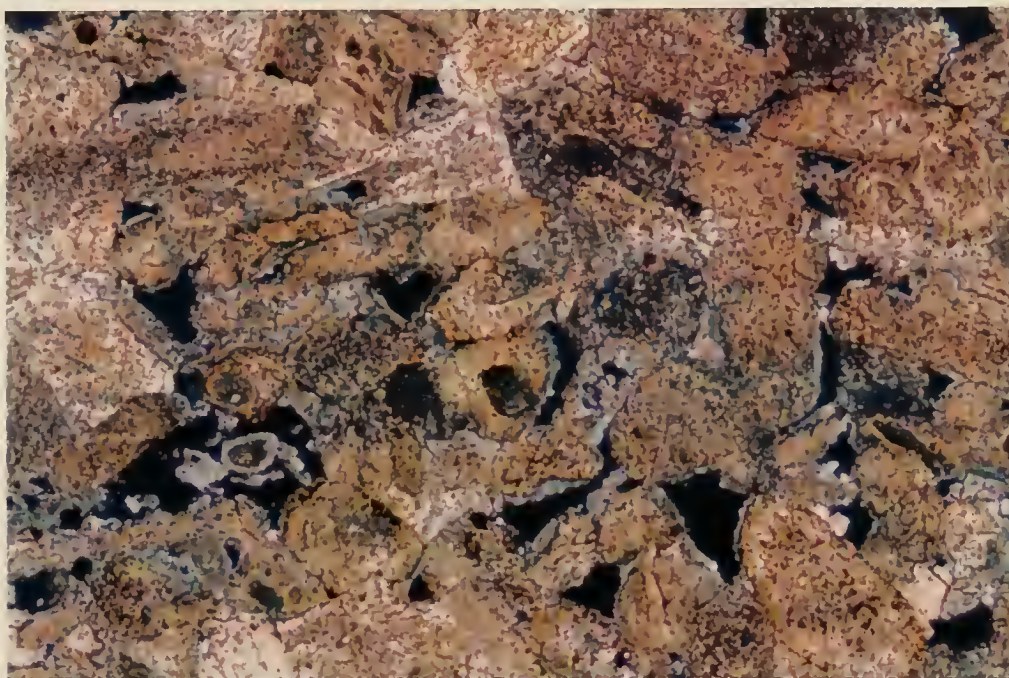
Figure 25: Indiana limestone before treatment, 25X, Note low number of pores and high quantity of allochems



Figure 26: Indiana limestone immersed in tap water, 50X, Note increase in pore space



Figure 27: Indiana limestone immersed in surfactant solution, 50X, Note increase in pore space



**Figure 28: Indiana limestone immersed in 34% herbicide solution, 50X,
Note loss of cement creating more pore space**

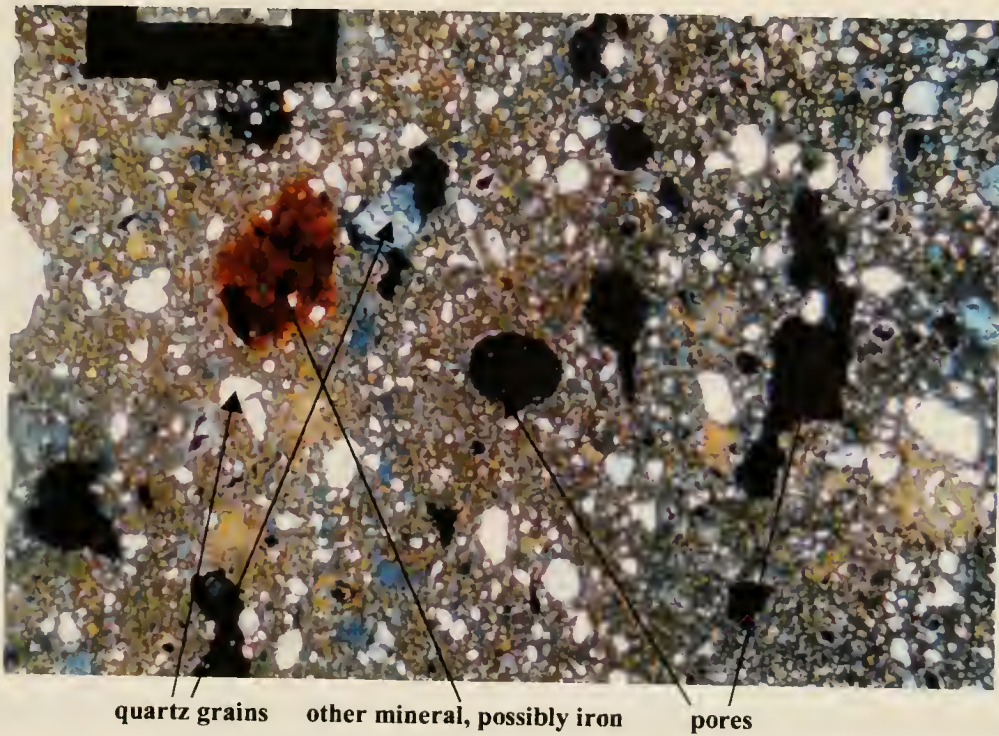


Figure 29: Fort Union brick before treatment, 25X

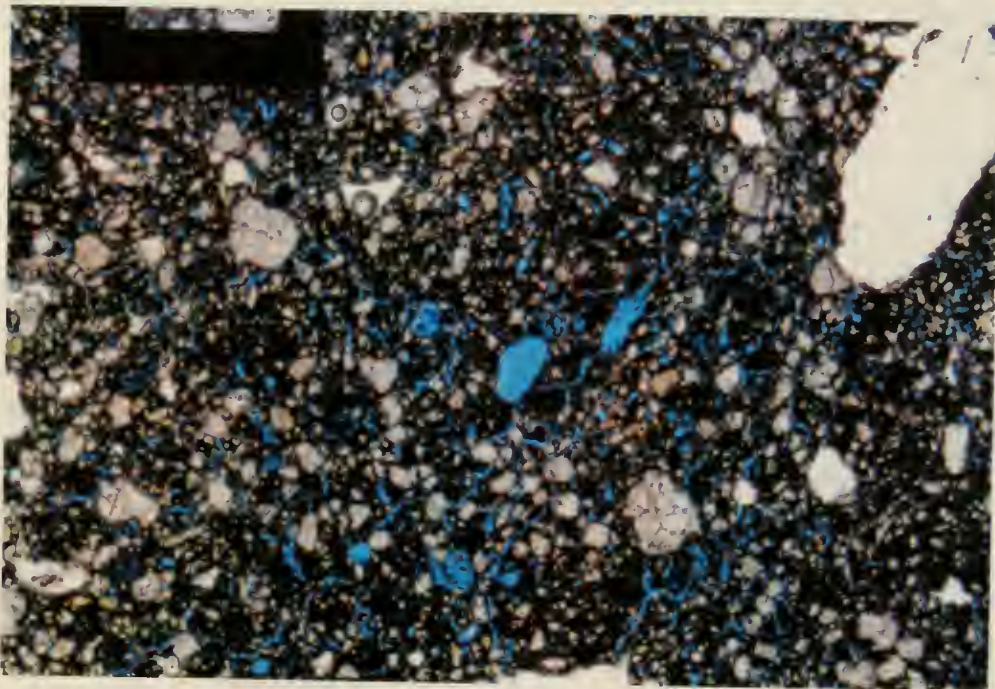


Figure 30: Fort Union brick immersed in tap water, 25X, Note small channels in clay matrix

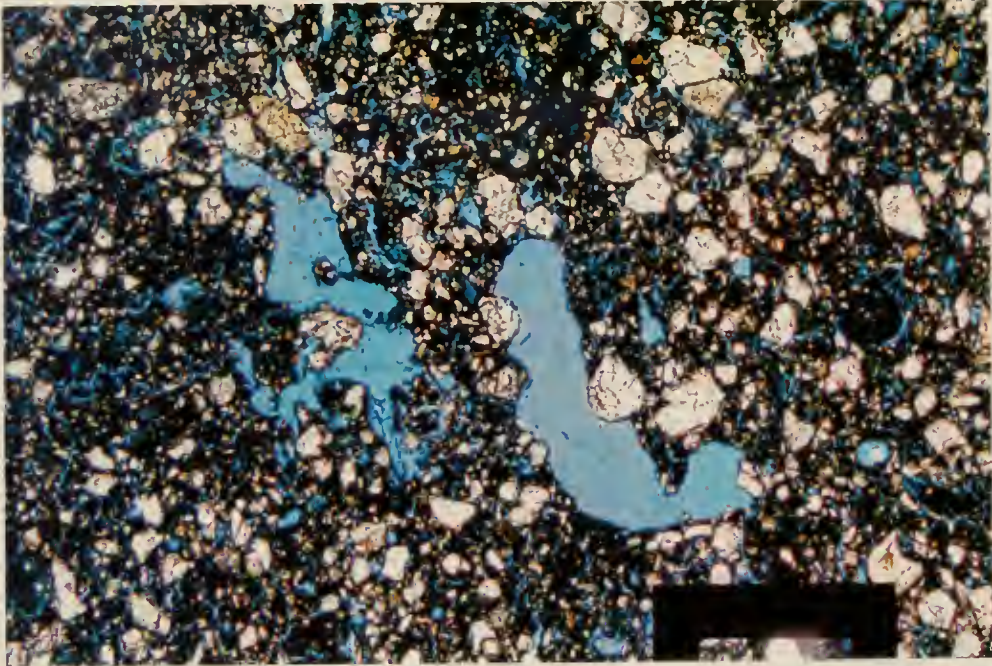


Figure 31: Fort Union Brick immersed in surfactant solution, 25X, Note small channels in clay matrix and pores similar to pre-treatment samples in size

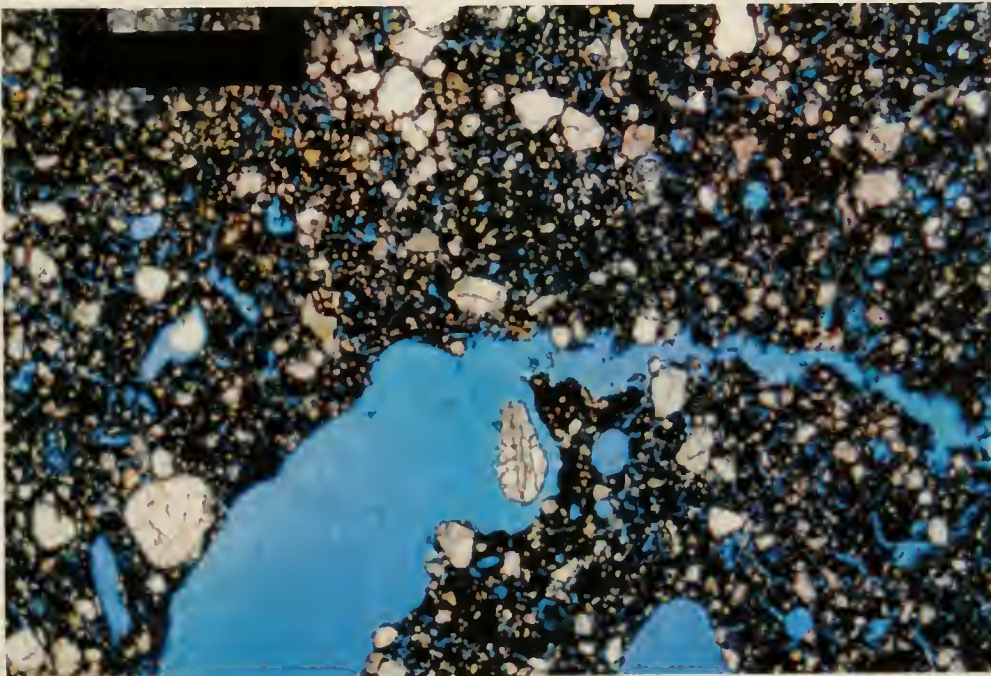


Figure 32: Fort Union brick immersed in 34% herbicide solution, 25X, Note formation of larger and smaller pores and channels

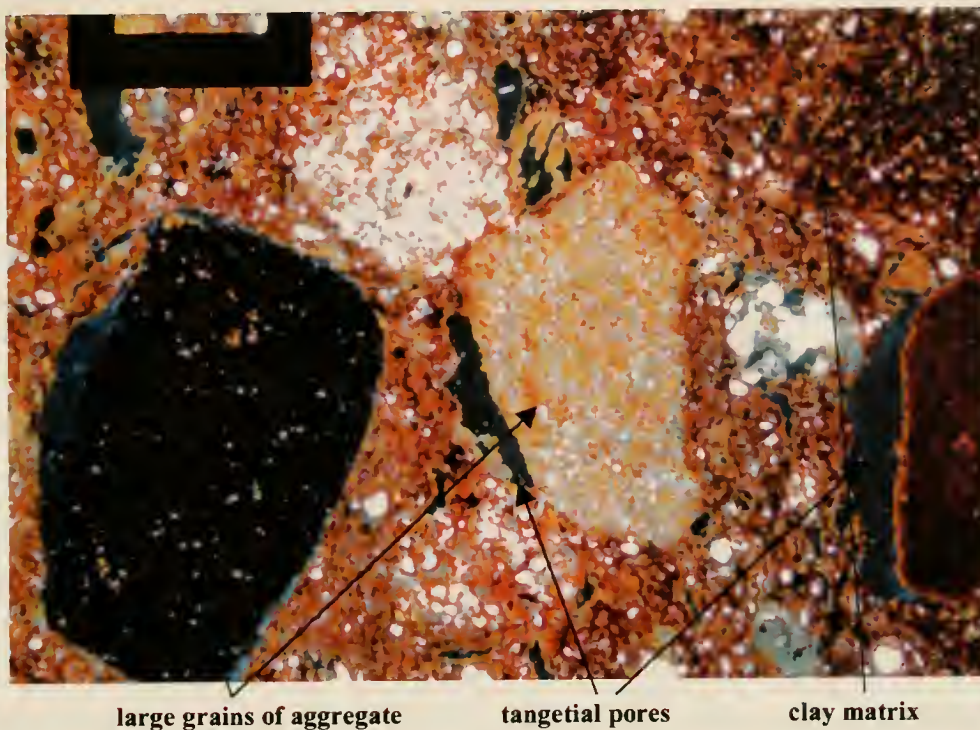


Figure 33: New brick before treatment, 25X

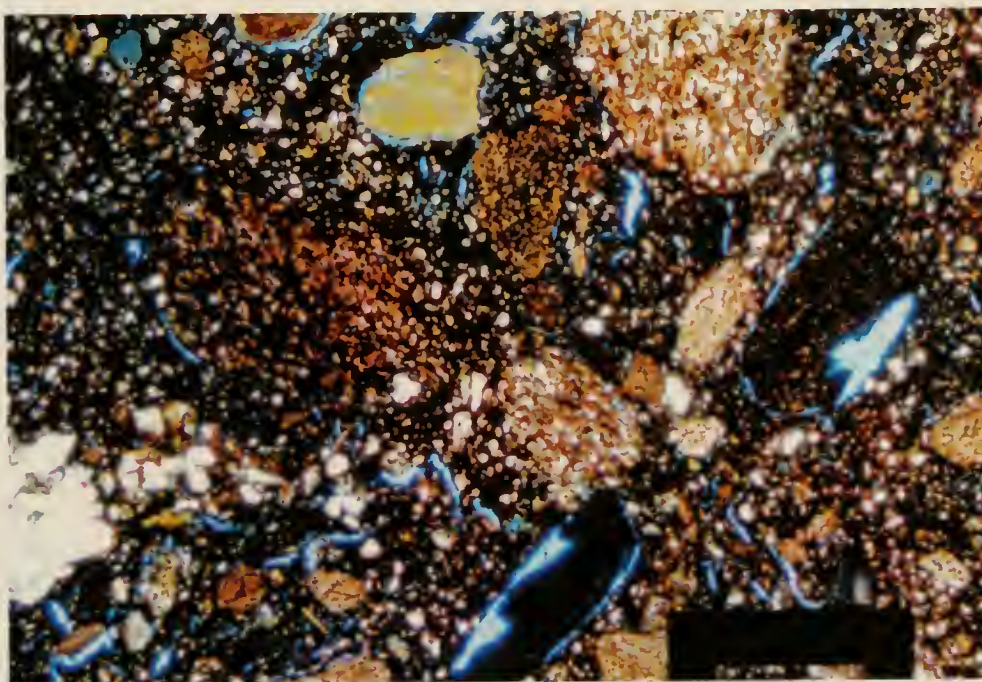


Figure 34: New brick immersed in 34% herbicide solution, 25X, Note little change in structure

Chapter Seven: Conclusions

In the realm of conservation, many chemical products have been adopted for use on historic sites, often without full consideration of the possible short or long term effects of the treatment. As a result, extensive damage may ensue. Common, commercially available treatments produced for a specific, desired result on standardized or modern materials may pose a serious threat to aged materials. This study demonstrates the need for review of all chemical products used on cultural heritage.

Herbicides were developed to control unwanted plants in an agricultural and later, residential context. Compared to labor intensive mechanical removal, herbicides provide an easy solution to the plant growth problem.

In this study, an examination of the potential damage from herbicide use on masonry structures was investigated. While the herbicide Round-up® is proven to kill weeds that damage and disfigure masonry, it cannot be used without some harmful alteration to the masonry. The damage to masonry caused by glyphosate is three-fold. It first attacks calcareous stone by acid dissolution. Secondly, it and its solvent, in this case water, introduce or redeposit soluble salts. Thirdly, in the presence of calcium -- a major component of building stones -- it forms insoluble salts.

The effect of the acidic glyphosate on the calcareous stone is the most disconcerting. It quickly destroys the stone's microstructure causing surface loss, and greater pore space. This will in turn affect the cohesive strength and

durability of the stone by weakening it and producing a more porous stone, which is susceptible to increased weathering. A secondary effect is the chromatic disfigurement caused by the acid. This will affect the aesthetic value of any monument or sculpture. Acids can also produce salts under the right conditions.

Salt deposits are also introduced from the use of regular water for the mixture of the herbicide. Although many masonry structures are affected by salts through other avenues, such as rising damp, rainfall and salts naturally found in the stone, there is no need to add salts to monuments.

Lastly the formation of insoluble salts is a major problem. It is unknown by the author if this is a trait of many herbicides or just Round-up[®]. By removing the calcium from carbonate stones to form the calcium-phosphate complex, the material is weakened, increasing its friability. Insoluble salts, in addition to affecting the durability of the stone, prohibit the release of water by obstructing the pores of the stone. Formation of insoluble as well as soluble salts are a danger especially if the herbicide is applied to a damp stone. Rainwater would be trapped inside the stone contributing to hydrostatic pressures. Insoluble salts are also a source of disfigurement and may cause damage to the stone by taking off layers of material during cleaning. Insoluble salts may also interfere with other conservation treatments.

Acidic herbicides have a much greater effect on natural stones especially calcareous ones, than on fired materials. This was confirmed by an acid susceptibility test on the samples. Both the calcareous sandstone and limestone

suffered extensive damage. Major surface loss was seen on both samples as well as intense color change on the limestone. Because of its high resistance to many chemicals, the bricks fared well under acidic conditions. This is reflected in the testing program as well. Unlike the calcareous stones, the bricks survived the acidic action of the herbicide suffering only, minor erosion and the formation of salts.

Acidic degradation, increase in salt content and color change are the major detrimental effects observed from the use of herbicides containing glyphosate. In addition to these detrimental effects, all post-emergent herbicides also leave dead plant remains which are unsightly and a haven for microorganisms.

Through the above testing program, several possible effects of glyphosate herbicides on masonry have been qualified. This is not to say that these are the only effects, nor that these effects will occur in every circumstance. More testing is needed to further evaluate other herbicides, a wider range of masonry materials and environmental conditions. Monitored in situ testing would be invaluable. The interactions between herbicides and other deterioration mechanisms such as rising damp or atmospheric soiling also require examination as well as possible interactions of residual herbicide and other conservation treatments.

After evaluating the deleterious effects of herbicides, several questions have been raised that can only be evaluated on individual sites. In many cases,

before the plants have reached maturity, mechanical removal is the best option. If the plants are pulled when their roots are small, potential mechanical damage to weak mortar joints and masonry units might be greatly reduced or eliminated. In the end, the effective management of unwanted macroflora at historic and archaeological sites will depend on many factors to determine the least harmful and most practical form of control.

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Table 1. Physical and chemical properties of glyphosate^a

		Remarks
Physical state	crystalline powder	
Colour	white	
Odour	none	
Melting point ^b	184.5 °C	decomposition at 187 °C
Boiling point	n.a.	
Specific gravity (density) ^c	1.704	20 °C
Vapour pressure ^d	$< 1 \times 10^{-5}$ Pa	25 °C
Solubility in water ^{b,e}	10 100 mg/litre	20 °C
Henry's law constant	$< 7 \times 10^{-11}$	
Octanol-water partition coefficient (log K_{ow}) ^d	-2.8	
Surface tension ^d	0.072 N/m	0.5% (w/v) at ~ 25 °C
pKa values ^{d,f}	< 2, 2.6, 5.6, 10.6	Sprankle et al. (1975)
Molar absorptivity ^c	0.086 litre/mol per cm	at 295 nm
Flammability ^d	not flammable	
Explosiveness ^d	not explosive	
pH ^d	2.5	1% solution

^a data provided by Monsanto Ltd

^b purity 96%

^c purity 100%

^d purity not reported

^e pure glyphosate had been reported to have a water solubility of 11 600 mg/litre at 25 °C

^f free acid

n.a. = not applicable

MONSANTO

MATERIAL SAFETY DATA

ROUNDUP® ULTRA herbicide

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MONSANTO PRODUCT NAME
ROUNDUP® ULTRA Herbicide

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION**Product Name:** ROUNDUP® ULTRA herbicide**Synonyms:** MON 65005**EPA Reg. No.:** 524-475**Company ID:** Monsanto Company
800 North Lindbergh
St. Louis, MO 63167, U.S.A.**Phone #s:** Emergency Phone Number (call collect): (314) 694-4000

Non-Emergency Information: 1-800-332-3111

Revisions: Sections containing a revision or new information are marked with a ♣**MSDS Number:** S00012770**Date:** May 21, 1997**Supersedes:** November, 1995**2. COMPOSITION INFORMATION ON INGREDIENTS****Chemical Ingredients:** *Active Ingredient:*Glyphosate, N-(phosphonomethyl) glycine,
in the form of its isopropylamine salt 41.0 %*Inert Ingredients:*

..... 59.0 %

100.0 %

Component**CAS Reg No****% wt in product**

Glyphosate, isopropylamine salt

38641-94-0

41.0%

No Hazardous Chemicals Under OSHA Hazard Communication Standard (29 CFR §1910.1200)

No components subject to the reporting requirements of SARA §313.

See Section 8 for exposure limits.**3. HAZARDS IDENTIFICATION****Emergency Overview:****Appearance & Odor:** Clear, viscous amber-colored solution**Warning Statements:** Keep out of reach of children.

CAUTION !

CAUSES EYE IRRITATION

REFORMULATION IS PROHIBITED

SEE INDIVIDUAL CONTAINER LABEL FOR REPACKAGING LIMITATIONS

Potential Adverse Health Effects:**Likely Routes of Exposure:** Skin contact and inhalation**Eye Contact:** ROUNDUP® ULTRA herbicide may cause pain, redness and tearing based on toxicity studies**Skin Contact:** ROUNDUP® ULTRA herbicide is no more than slightly toxic and no more than slightly irritating based on toxicity studies.**MSDS #:** S00012770**May 21, 1997**

MONSANTO**MATERIAL SAFETY DATA****ROUNDUP® ULTRA herbicide**

Page 2 of 6

- Ingestion:** ROUNDUP® ULTRA herbicide is no more than slightly toxic based on toxicity studies. No significant adverse health effects are expected to develop if only small amounts (less than a mouthful) are swallowed. Ingestion of similar formulations has been reported to produce gastrointestinal discomfort with irritation of the mouth, nausea, vomiting and diarrhea. Oral ingestion of large quantities of one similar product has been reported to result in hypotension and lung edema.
- Inhalation:** ROUNDUP® ULTRA herbicide is no more than slightly toxic if inhaled based on toxicity studies.

4. FIRST AID MEASURES

If In Eyes: Flush with plenty of water. Get medical attention if irritation persists.

NOTE: For additional human emergency first aid or treatment guidance, call collect, anytime, day or night (314) 694-4000.

5. FIRE FIGHTING MEASURES ♣

Flash Point: None

Hazardous Combustion Products: CO, CO₂, Nox

Auto Ignition Temperature: Not determined

Extinguishing Media: Water spray, foam, dry chemical, CO₂, or any class B extinguishing agent.

Special Fire Fighting Procedures: Firefighters and others that may be exposed to vapors, mists, or products of combustion should wear full protective clothing and self-contained breathing apparatus. Equipment should be thoroughly cleaned after use.

Unusual Fire or Explosion Hazards: None

6. ACCIDENTAL RELEASE MEASURES

Observe all protection and safety precautions when cleaning up spills - See Exposure Controls/Personal Protection, Section 8

Small Spills: For a spill less than one gallon on floor or other impervious surface, soak up with towels or other absorbent material and discard in the trash. Clean the spill area with soap and water and rinse the area thoroughly.

Large Liquid Spills on the floor or other impervious surface should be contained or diked and then absorbed with attapulgite, bentonite or other absorbent clays. Collect the contaminated absorbent, place in a metal drum and dispose of in accordance with the instructions provided under Disposal, Section 13 of this MSDS. Thoroughly scrub floor or other impervious surface with a strong industrial detergent and rinse with water.

Large spills that soak into the ground should be dug up, placed in metal drums and disposed of in accordance with instructions provided under DISPOSAL, Section 13 of this MSDS. Contact appropriate state agency when considering a land spreading disposal option.

Leaking containers should be separated from non-leakers and either the container or its contents transferred to a drum or other non-leaking container and disposed of in accordance with instructions provided under DISPOSAL, Section 13 of this MSDS. Any recovered spilled liquid should be similarly collected and disposed of.

MONSANTO

MATERIAL SAFETY DATA

ROUNDUP® ULTRA herbicide

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7. HANDLING AND STORAGE**Handling:**

- Avoid contact with eyes or clothing.
- Wash hands before eating, drinking, chewing gum, using tobacco, or using the toilet.
- Remove clothing immediately if pesticide gets inside. Then wash thoroughly and put on clean clothing.
- Do not apply directly to water, to areas where surface water is present or to intertidal areas below the mean high water mark.
- Do not contaminate water when disposing of equipment washwaters.

Storage:

- Do not contaminate water, foodstuffs, feed or seed by storage or disposal.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION**Personal Protective Equipment:**

Eye Protection: Workers handling the packaged concentrate should wear chemical safety goggles to prevent eye contact during mixing/transfer operations or other activities where there is potential for eye contact with the concentrated product. The wearing of goggles is not required during use of this product in accordance with label instruction.

Skin Protection: Wear appropriate protective clothing to prevent skin contact. Applicators and other handlers must wear long-sleeved shirt, long pants, shoes plus socks. Follow manufacturer's instructions for cleaning/maintaining PPE. If no such instructions for washables, use detergent and hot water. Keep and wash PPE separately from other laundry.

Respiratory Protection: For Handling the Concentrated Product: Avoid breathing vapor or mist. This product concentrate is not likely to pose an airborne exposure concern during manufacture or packaging. In the event of abnormal exposure conditions, use NIOSH/MSHA approved equipment. In work situations where an air purifying respirator is appropriate to be used, use of a full face respirator equipped with purifying elements for protection against organic vapor and dust/mist approved for pesticides is recommended. Use cartridges with NIOSH/MSHA approval number TC-23C or canister with NIOSH/MSHA approval number TC-14G. Full facepiece replaces the need for chemical goggles. Observe respirator use limitations specified by the manufacturers. Respiratory protection programs must comply with 29 CFR 1910.134.

For Use of Product in accordance with label instructions: Respirators are not required for use of ROUNDUP® ULTRA herbicide in accordance with label instructions.

Ventilation: No special precautions are recommended.

Exposure Guidelines:	<u>Exposure Limits</u>	<u>OSHA PEL</u>	<u>ACGIH TLV</u>
	ROUNDUP® ULTRA	None established	None established

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance: clear, viscous amber-colored solution
Odor: practically odorless to slight amine-like odor
Ph: 4.99 (1% solution)
Specific Gravity: 1.17 (Water = 1)

Note: These physical data are typical values based on material tested but may vary from sample to sample. Typical values should not be construed as a guaranteed analysis of any specific lot or as specification items.

MONSANTO MATERIAL SAFETY DATA ROUNDUP® ULTRA herbicide Page 4 of 6

10. STABILITY AND REACTIVITY

Chemical Stability:	Stable for at least 5 years under normal conditions of warehouse storage.
Conditions to Avoid:	None
Incompatibility with Other Materials:	<p>Spray solutions of this product should be mixed, stored or applied using only stainless steel, aluminum, fiberglass, plastic or plastic-lined containers.</p> <p>DO NOT MIX, STORE OR APPLY THIS PRODUCT OR SPRAY SOLUTIONS OF THIS PRODUCT IN GALVANIZED OR UNLINED STEEL (EXCEPT STAINLESS STEEL) CONTAINERS OR SPRAY TANKS. This product or spray solutions of this product react with such containers and tanks to produce hydrogen gas which may form a highly combustible gas mixture. This gas mixture could flash or explode, causing serious personal injury, if ignited by open flame, spark, welder's torch, lighted cigarette or other ignition source.</p>
Hazardous Decomposition Products:	None
Hazardous Polymerization:	Does not occur. This product can react with caustic (basic) materials to liberate heat. This is not a polymerization but rather a chemical neutralization in an acid base reaction.

11. TOXICOLOGICAL INFORMATION

Data from laboratory studies conducted by Monsanto with ROUNDUP® ULTRA herbicide are summarized below:

Single exposure (acute) studies indicate:

Oral -	Rat LD ₅₀ - >5,000 mg/kg, FIFRA Category IV
Dermal -	Rat LD ₅₀ - >5,000 mg/kg, FIFRA Category IV
Inhalation -	Rat LC ₅₀ (4-hr. exp.) - 4.2 mg/l; FIFRA Category IV, Not DOT poisonous
Eye Irritation -	Rabbit: moderately irritating.; all animals free of irritation by day 7, FIFRA Category III
Skin Irritation -	Rabbit (4-hr. exp.): slightly irritating; PII - 0.63/8.0, all animals free of irritation by day 7, FIFRA Category IV

No skin allergy was observed in guinea pigs following repeated skin exposure.

COMPONENTS

Data from laboratory studies conducted by Monsanto and from the scientific literature on components of ROUNDUP® ULTRA herbicide:

Isopropylamine Salt of Glyphosate

Data from studies with a formulation comprised of 62% isopropylamine salt of glyphosate (MON 0139) indicate the following:

In repeat dosing studies (6-month), dogs fed MON 0139 exhibited slight body weight changes. Following repeated skin exposure (3-week) to MON 0139, skin irritation was the primary effect in rabbits.

Additional toxicity information is available on glyphosate, the active herbicidal ingredient of MON 0139. Following repeated exposures (90-days) to glyphosate in their feed, decreased weight gains were

MONSANTO**MATERIAL SAFETY DATA****ROUNDUP® ULTRA herbicide**

Page 5 of 6

noted at the highest test level in mice, while no treatment-related effects occurred in rats. Following repeated skin exposure (3 weeks) to glyphosate, slight skin irritation was the primary effect observed in rabbits. No skin allergy was observed in guinea pigs following repeated skin exposure. There was no evidence of effects on the nervous system, including delayed effects in chickens (repeat oral doses) or cholinesterase inhibition in rats (single oral doses). Reduced body weight gain and effects on liver tissues were observed with long-term (2-year) feeding of glyphosate to mice at high-dose levels. Reduced body weight gain and eye changes were observed at the high-dose level in one long-term (2 year) feeding study with rats, while no treatment-related effects occurred in a second study. No adverse effects were observed in feeding studies with dogs. Glyphosate did not produce tumors in any of these studies. **Based on the results from the chronic studies, EPA has classified glyphosate in category E (evidence of non-carcinogenicity for humans).** No birth defects were noted in rats and rabbits given glyphosate orally during pregnancy, even at amounts which produced adverse effects on the mothers. Glyphosate was fed continuously to rats at very high dose levels for 2 successive generations. Toxicity was reported in offspring from the high dose, a level which also produced adverse effects on the mothers. In a 3 generation study conducted at lower dose levels, no effects were seen on the ability of male or female rats to reproduce. Glyphosate has produced no genetic changes in a variety of standard tests using animals and animal or bacterial cells.

12. ECOLOGICAL INFORMATION

Aquatic and Avian studies with this product have not been conducted at this time. However, an extensive database of studies exists for the active ingredient glyphosate. These studies indicate that glyphosate ranges from practically non-toxic to slightly toxic in a variety of aquatic and avian species. For glyphosate MSDS or additional information, contact Monsanto at 1-800-332-3111.

13. DISPOSAL CONSIDERATIONS

Wastes resulting from the use of this product that cannot be used or chemically reprocessed should be disposed of in a landfill approved for pesticide disposal or in accordance with applicable Federal, state or local procedures.

Emptied container retains vapor and product residue. Observe all labeled safeguards until container is cleaned, reconditioned or destroyed.

14. TRANSPORT INFORMATION

Follow the precautions indicated in the Handling and Storage Section, Section 7 of this MSDS.

DOT Proper Shipping Name: Not Applicable

DOT Hazard Class/I.D. No.: Not Applicable

DOT Label: Not Applicable

U.S. Surface Freight Classification: Weed killing compound, N.O.I.B.N.

15. REGULATORY INFORMATION

SARA Hazard Notification:

Hazard Categories Under Criteria of SARA Title III Rules (40 CFR Part 370): Immediate

Section 313 Toxic Chemical(s): Not Applicable

MSDS #: S00012770

May 21, 1997

Sample Schedule

The samples were divided by type, and numbered according to the solutions in which they were to be immersed.

Sample number	Solution
Sample 1	34% herbicide solution
Sample 2	34% herbicide solution
Sample 3	34% herbicide solution
Sample a	17% herbicide solution
Sample b	17% herbicide solution
Sample c	17% herbicide solution
Sample A	Surfactant solution
Sample B	Surfactant solution
Sample C	Surfactant solution
Sample R	Tap water
Sample I	Tap water
Sample T	Tap water

Water Absorption: Pre-treatment**San Juan Sandstone**

Samples	Dry weight	5 min	30 min	60 min	8 hours	24 hours	48 hours	72 hours
1	310.11	340.88	341.17	341.58	342.4	342.67	344.61	346
2	261.5	298.5	297.67	297	295.62	296.64	297.77	299.11
3	278.15	305.36	304.11	304.99	303.5	305	306.78	307.21
A	300.08	337.27	336.19	335.47	335.16	335.63	336.84	337.58
B	266.98	296.57	295.62	295.07	294.78	294.48	296.3	296.92
C	225.85	245.7	245.33	244.73	244.32	244.19	245.26	245.97
a	307.72	340.88	339.28	340.99	341.56	342.41	345.33	344.91
b	285.23	324.16	323.21	322.42	322.22	322.28	324.26	323.66
c	270.92	292.58	292.49	292.92	292.36	292.57	294.08	295
R	276.17	299.71	292.78	293.77	292.79	293.8	295.07	295.21
I	273.62	315.94	315.61	315.61	315.52	316.84	318.35	319.22
T	309.27	341.62	342.37	342.22	342.36	343.51	344.93	345.13

Indiana Limestone

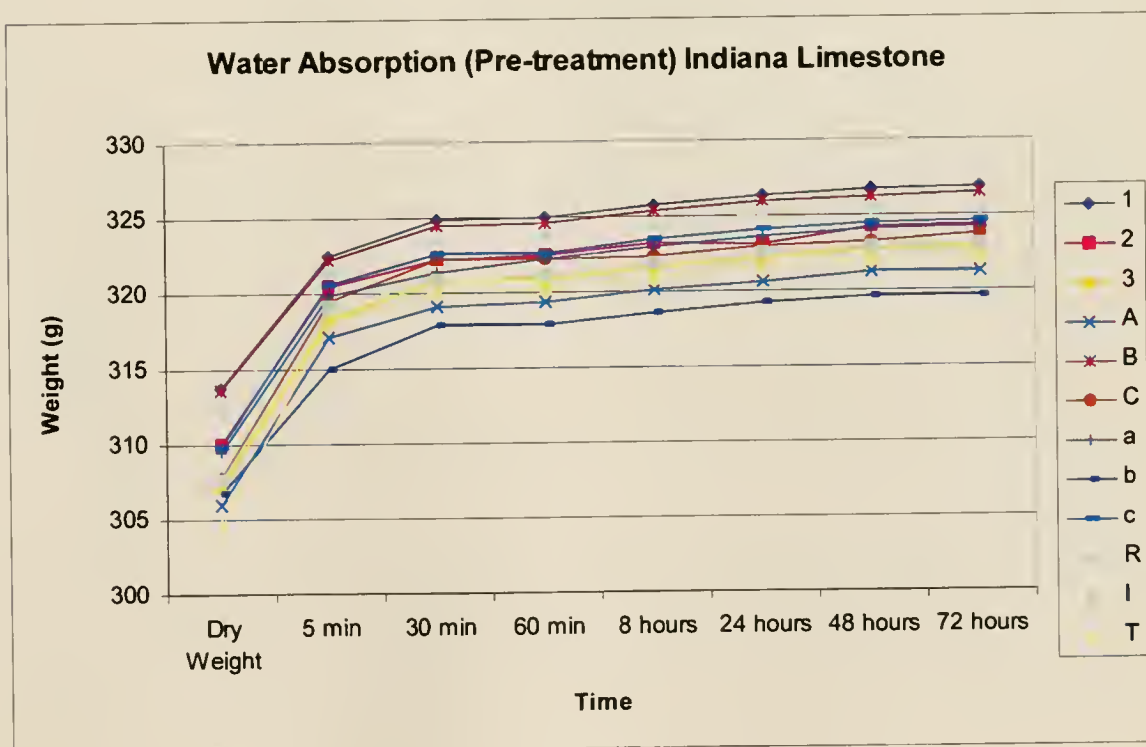
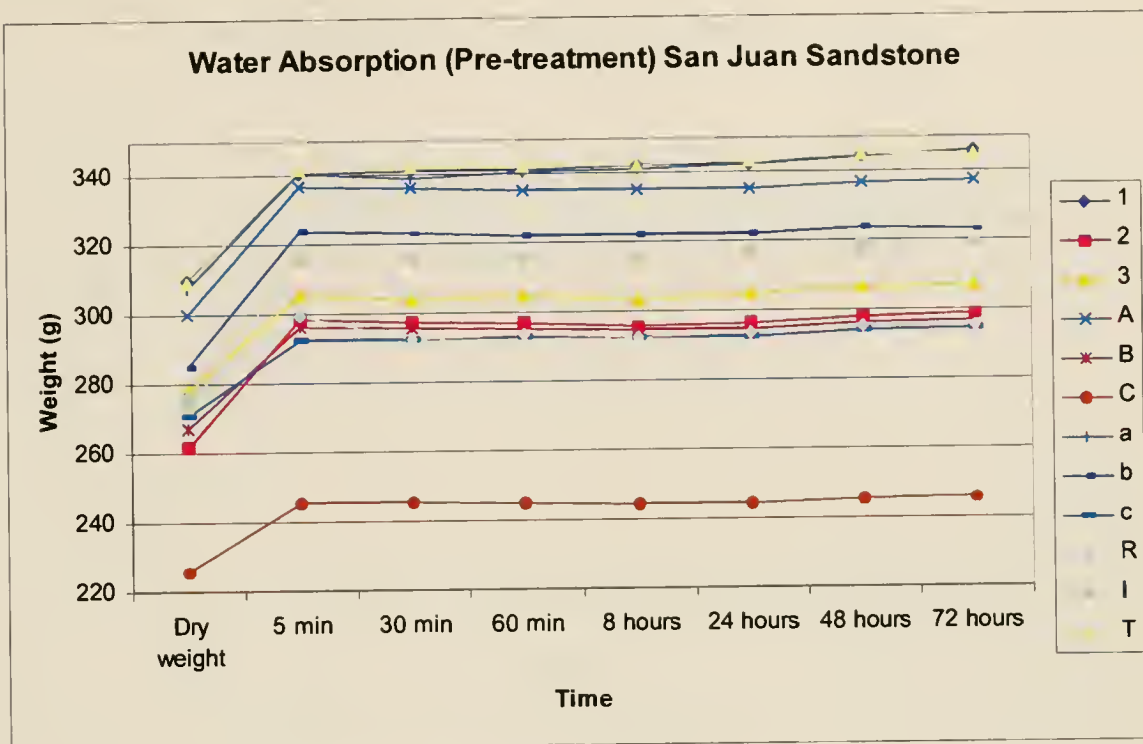
Samples	Dry Weight	5 min	30 min	60 min	8 hours	24 hours	48 hours	72 hours
1	313.71	322.47	324.89	325	325.8	326.42	326.73	326.83
2	309.98	320.46	322.3	322.46	323.21	323.09	324.29	324.36
3	307.3	318.3	320.88	320.9	321.68	322.3	322.74	322.87
A	306.01	317.13	319.16	319.4	320.1	320.67	321.23	321.3
B	313.63	322.26	324.45	324.64	325.38	325.96	326.24	326.55
C	307.77	319.55	322.21	322.24	322.32	322.99	323.31	323.71
a	309.55	319.83	321.41	322.24	323.01	323.65	324.1	324.21
b	306.8	315.06	317.86	317.9	318.57	319.25	319.61	319.67
c	309.88	320.66	322.57	322.68	323.49	324.12	324.48	324.58
R	311.94	321.36	323.5	323.75	324.43	325.07	325.36	325.4
I	307.58	319.12	320.93	321.12	321.85	322.52	322.85	323.01
T	304.6	318.07	320.08	320.28	320.91	321.59	321.97	322.12

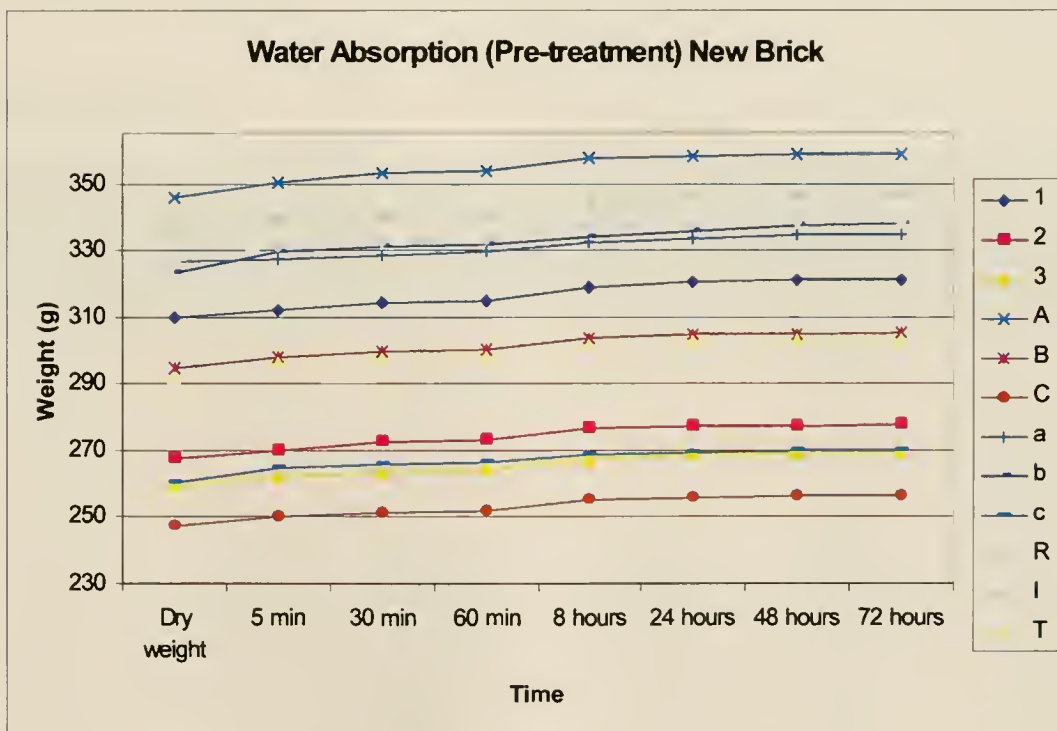
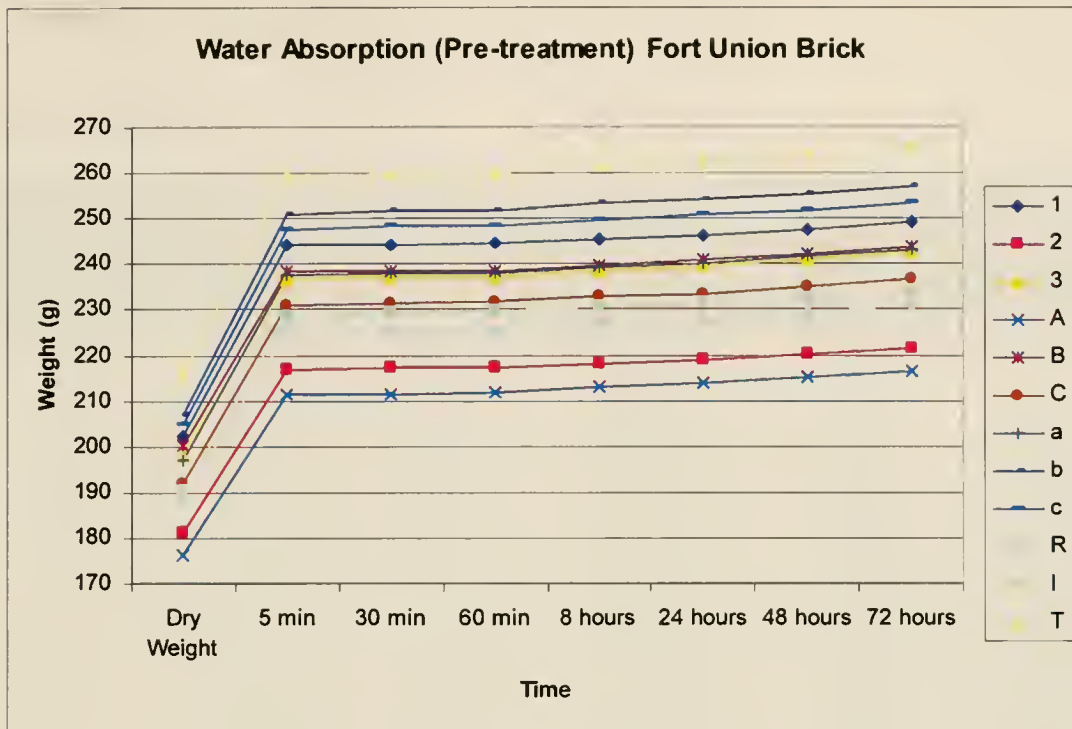
Water Absorption: Pre-treatment**Fort Union Brick**

Samples	Dry Weight	5 min	30 min	60 min	8 hours	24 hours	48 hours	72 hours
1	202.39	244.24	244.45	244.62	245.7	246.53	247.64	249.34
2	181	216.85	217.16	217.22	218.27	219.15	220.32	221.49
3	197.71	236.74	237.08	237.22	238.59	239.77	241.12	242.8
A	176.35	211.46	211.51	211.74	213	213.99	215.06	216.63
B	200.12	238.4	238.51	238.55	239.84	241.01	242.29	244.01
C	192.1	231.17	231.45	231.66	232.87	233.45	235.01	236.65
a	197.05	237.51	237.88	238.05	239.17	240.27	241.61	242.89
b	206.93	250.86	251.61	251.72	253.25	254.43	255.45	257.23
c	204.93	247.71	248.39	248.48	249.74	250.78	251.82	253.25
R	188.61	225.32	225.56	225.74	226.86	227.75	229.28	230.98
I	190.15	228.65	229.35	229.59	230.64	231.55	232.4	233.4
T	216.23	259.35	259.87	260.24	261.52	262.6	263.99	265.86

New Brick

Samples	Dry weight	5 min	30 min	60 min	8 hours	24 hours	48 hours	72 hours
1	309.69	312	314.45	314.93	318.87	320.43	320.95	321.07
2	267.91	269.72	272.76	273.58	276.48	277.1	277.51	277.59
3	259.49	261.95	263.43	264.23	267.28	268.65	269.03	269.12
A	345.95	350.55	352.92	353.91	357.6	358.24	358.8	358.96
B	294.78	297.92	299.89	300.47	303.76	304.67	305	305.21
C	247.5	250.12	251.62	251.93	255.24	256.06	256.45	256.67
a	326.48	327.22	328.71	329.38	332.27	333.54	334.45	334.77
b	323.6	329.74	331.29	331.76	334.1	335.86	337.5	338.09
c	260.46	264.68	266.18	266.6	268.71	269.64	269.99	270.19
R	326.94	331.37	333.03	333.6	336.87	338.21	338.62	338.84
I	335.52	338.38	339.67	340.4	344.57	346.12	346.41	346.64
T	292.1	296.43	297.61	297.97	301.29	302.69	303.06	303.39





Porosity: Pre-treatment

San Juan Sandstone

Samples	Mo (initial mass)	Mmax (mass of saturated sample)	Mp (Vp) Mass of pores (Mmax-Mo)	Va (apparent volume)	% porosity
1	310.11	346.00	35.89	175	20.5
2	261.50	299.11	37.61	150	25.1
3	278.15	307.21	29.06	160	18.2
A	300.08	337.58	37.5	160	23.4
B	266.98	292.92	29.94	150	20.0
C	225.85	245.97	20.12	130	15.6
a	307.72	344.91	37.19	170	21.9
b	285.23	323.66	38.43	170	22.6
c	270.92	295.00	24.08	145	16.6
R	273.62	295.21	21.59	150	14.3
I	276.49	319.22	42.73	160	26.7
T	309.27	345.13	35.86	170	21.1

Indiana Limestone

Samples	Mo (initial mass)	Mmax (mass of saturated sample)	Mp (Vp) Mass of pores (Mmax-Mo)	Va (apparent volume)	% porosity
1	313.71	326.83	13.12	140	9.4
2	309.98	324.36	14.38	140	10.3
3	307.30	322.87	15.57	140	11.1
A	306.01	321.30	12.92	140	10.9
B	313.63	326.55	12.92	140	9.2
C	307.77	323.71	15.94	140	11.4
a	309.55	324.21	14.66	140	10.5
b	304.60	319.67	15.07	140	10.8
c	309.88	324.58	14.70	140	10.5
R	307.58	325.40	17.82	140	12.7
I	311.94	323.01	11.07	140	7.9
T	306.80	322.12	15.32	140	10.9

Porosity: Pre-treatment

Fort Union Brick

Sample	Mo (initial mass)	Mmax (mass of saturated sample)	Mp (Vp) Mass of pores (Mmax-Mo)	Va (apparent volume)	% porosity
1	202.39	249.34	46.95	140	33.5
2	181.00	221.49	40.49	120	33.7
3	197.71	242.80	45.09	140	32.2
A	176.35	216.63	40.28	125	32.2
B	200.12	244.01	43.89	125	35.1
C	192.10	236.65	44.55	125	35.6
a	197.05	242.89	45.84	140	32.7
b	206.93	257.23	50.3	145	34.7
c	204.93	253.25	48.32	145	33.3
R	190.15	230.98	40.83	130	31.4
I	188.61	233.40	44.79	120	37.3
T	216.23	265.86	49.63	150	33.1

New Brick

Sample	Mo (initial mass)	Mmax (mass of saturated sample)	Mp (Vp) Mass of pores (Mmax-Mo)	Va (apparent volume)	% porosity
1	309.69	321.07	11.38	140	8.1
2	267.48	277.59	10.11	110	9.2
3	259.49	269.12	9.63	110	8.8
A	245.49	358.96	13.01	150	8.7
B	294.78	305.21	10.43	125	8.3
C	247.50	256.67	9.17	100	9.2
a	326.48	334.77	8.29	150	5.5
b	323.60	338.09	14.49	140	10.4
c	260.46	270.19	9.73	110	8.8
R	335.32	346.64	11.32	140	8.1
I	326.94	338.84	11.9	140	8.5
T	292.49	303.39	10.51	120	8.6

Water Absorption: Post-treatment**San Juan Sandstone**

Samples	Dry weight	5 min	30 min	60 min	8 hours	24 hours	48 hours	72 hours
1	310.54	346.96	347.61	347.78	349.12	350.25	350.91	353.23
2	261.43	286.32	291.89	293.72	297.45	297.76	297.26	299.1
A	298.89	332.38	334.56	335.2	335.25	336.54	335.66	336.29
B	266.28	293.2	296.53	296.91	297.7	296.6	297.49	297.67
a	307.34	346.01	346.95	347.21	346.58	346.29	346.33	346.75
b	284.44	317.7	320.02	321.43	325.69	326.09	325.66	326.46
c	270.79	291.93	292.41	293.43	293.76	294.27	294.45	296.22
I	272.94	319.63	319.03	318.9	318.58	318.15	318.47	320.16
T	308.34	341.36	342.67	342.75	344.11	343.48	344.4	345.94

Indiana Limestone

Samples	Dry weight	5 min	30 min	60 min	8 hours	24 hours	48 hours	72 hours
1	314.28	315.37	317.2	318.85	324.82	325.33	325.5	325.77
3	307.85	309.58	312.7	315.06	320.93	321.11	321.26	321.47
B	313.64	318.85	321.4	322.66	324.01	324.33	324.49	324.86
C	307.84	315.07	318.65	320.31	321.16	321.36	321.63	321.84
a	309.43	312.29	317.26	320.48	321.94	322.14	322.37	322.68
b	306.68	311	315.78	318.38	320.04	320.18	320.46	320.78
c	309.6	312.04	315.99	318.85	322.24	322.38	322.68	323.08
I	307.43	317.92	320.42	320.49	320.84	321.1	321.46	321.73
T	304.49	314.57	317.3	317.41	317.79	318.09	318.41	318.63

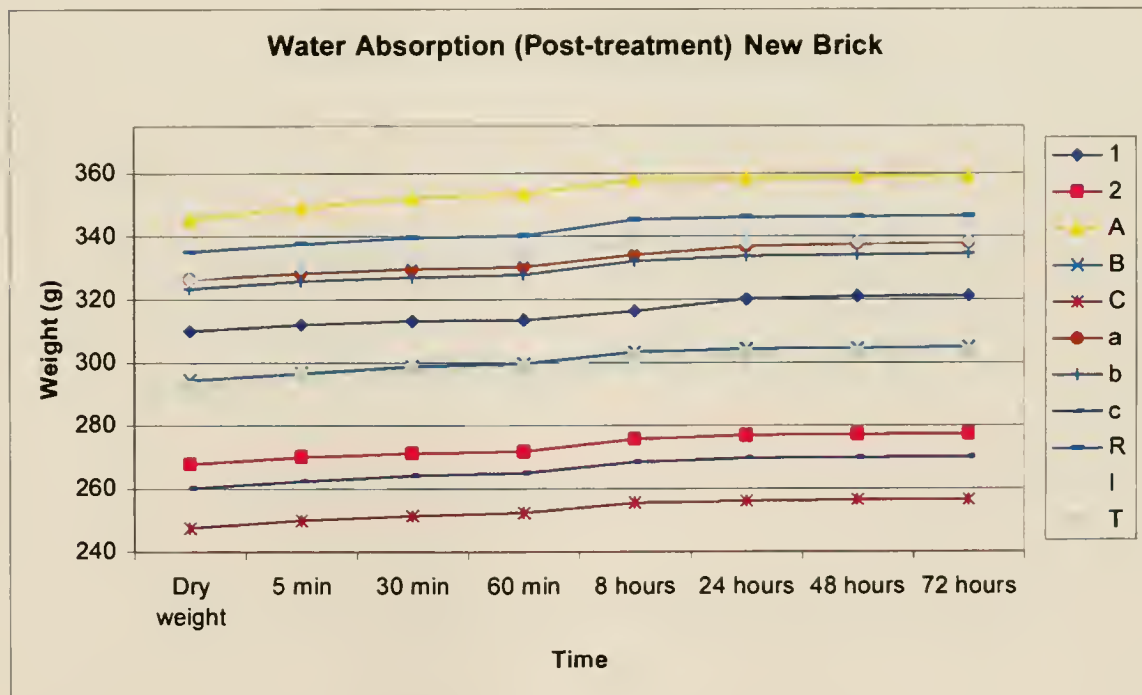
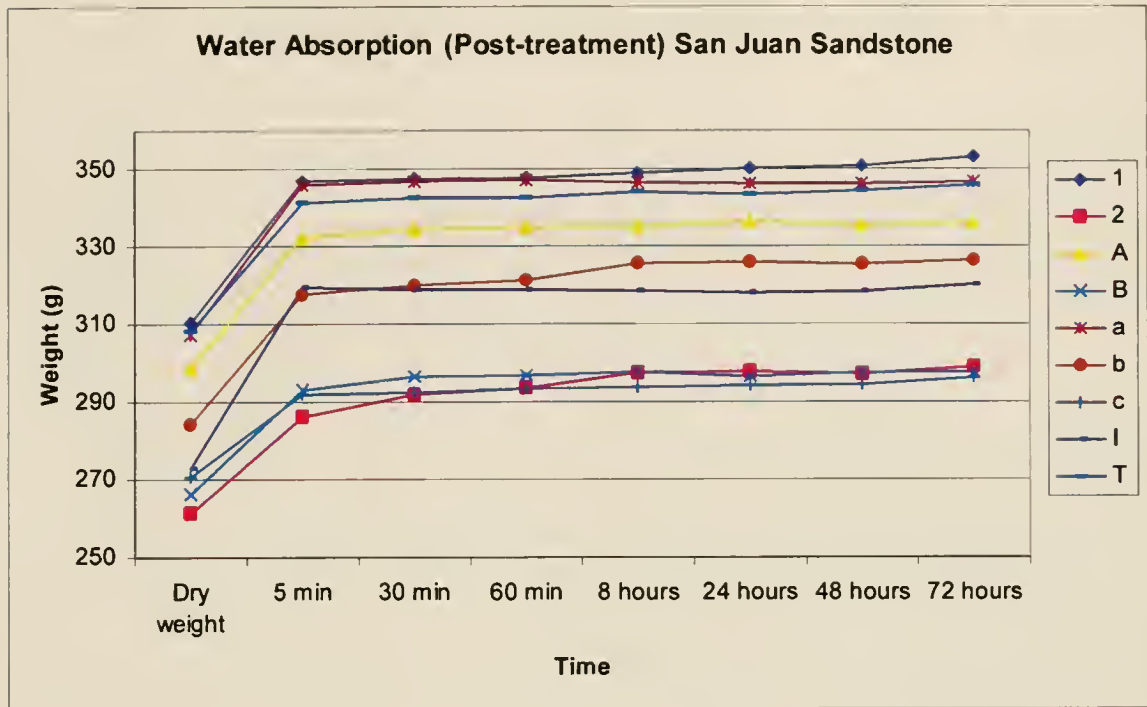
Water Absorption: Post-treatment

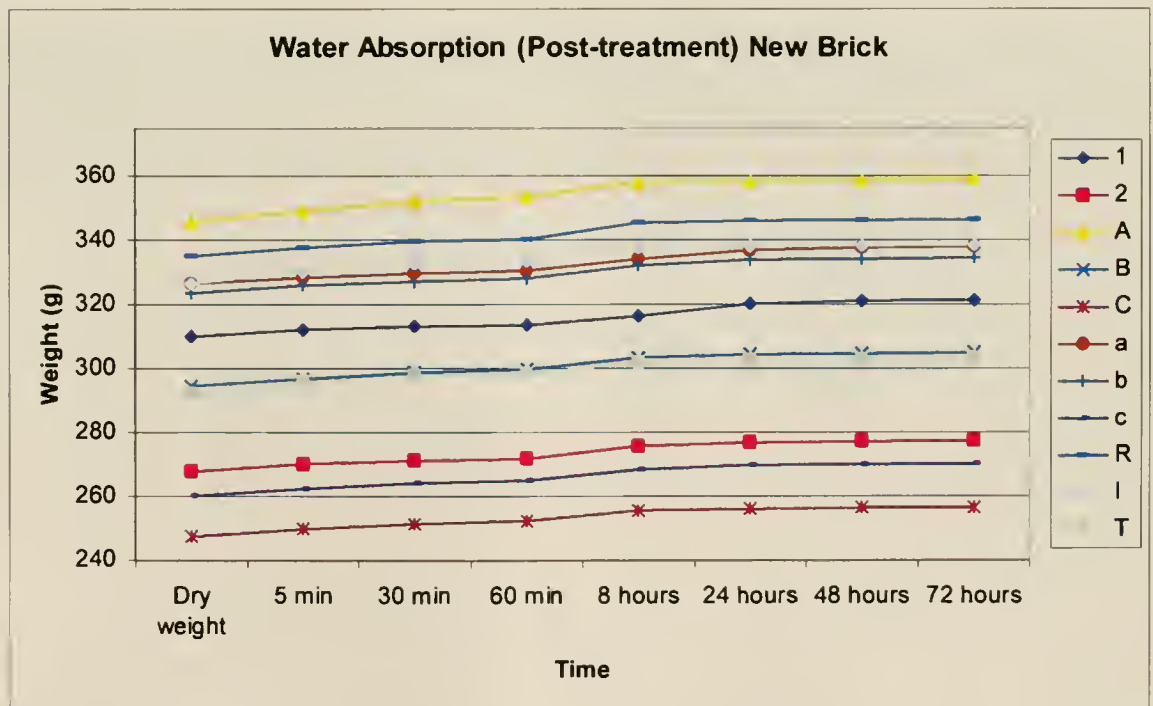
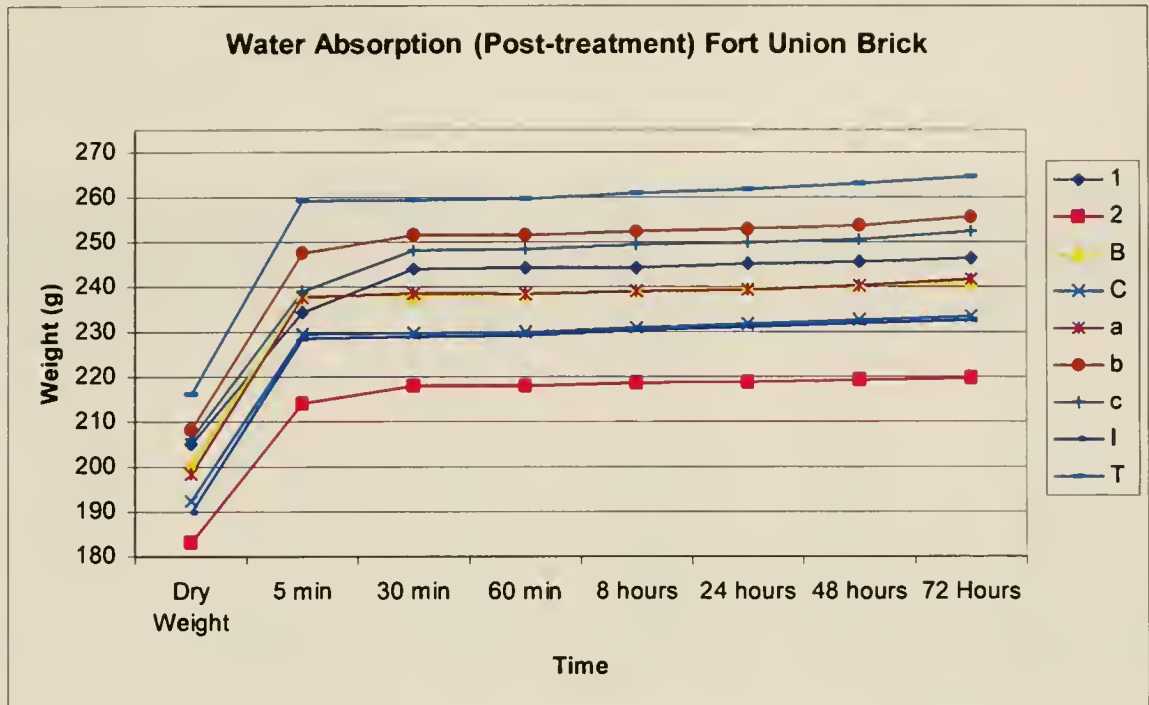
Fort Union Brick

Samples	Dry Weight	5 min	30 min	60 min	8 hours	24 hours	48 hours	72 hours
1	205.07	234.36	243.99	244.23	244.27	245.16	245.52	246.34
2	183.21	214.17	217.97	217.99	218.61	218.81	219.3	219.74
B	200.27	238.05	237.96	238.27	238.96	239.63	240.28	241.02
C	192.34	229.46	229.71	230	230.96	231.64	232.61	233.48
a	198.43	237.75	238.46	238.36	239	239.34	240.26	241.72
b	208.2	247.51	251.59	251.56	252.32	252.85	253.65	255.55
g	206.09	239.09	248.13	248.3	249.36	249.78	250.5	252.3
l	189.89	228.44	228.85	229.11	230.41	231.02	231.87	232.63
T	216.14	259.09	259.28	259.53	260.85	261.73	263.05	264.64

New Brick

Samples	Dry weight	5 min	30 min	60 min	8 hours	24 hours	48 hours	72 hours
1	309.96	312.1	313.29	313.67	316.36	320.23	321.09	321.23
2	267.92	270.08	271.24	271.91	275.81	276.97	277.27	277.45
A	345.51	349.1	352.12	353.5	358.05	358.4	358.74	359.03
B	294.4	296.8	298.83	299.78	303.36	304.32	304.67	304.9
C	247.44	249.92	251.43	252.3	255.61	256.17	256.41	256.55
a	326.47	328.43	329.75	330.47	334.21	336.82	337.76	338.03
b	323.46	325.99	327.1	327.96	332.04	333.87	334.27	334.47
c	260.21	262.46	264.19	265.15	268.43	269.72	270.03	270.23
R	335.15	337.71	339.59	340.32	345.45	346.21	346.39	346.57
l	326.58	330.21	332.76	333.7	337.7	338.03	338.23	338.52
T	292.07	295.82	297.85	298.47	301.8	302.8	302.86	303.21





Porosity: Post-treatment

San Juan Sandstone

Sample	Mo (initial mass)	Mmax (mass of saturated sample)	Mp (Vp) Mass of pores (Mmax-Mo)	Va (apparent volume)	% porosity
1	310.54	353.23	42.69	175	24.4
2	261.43	299.10	37.67	150	25.1
A	298.89	336.29	37.4	160	23.4
B	266.28	297.67	31.39	150	20.9
a	307.34	346.75	39.41	170	23.2
b	284.44	326.46	42.02	170	24.7
c	270.79	296.22	25.43	145	17.5
I	272.94	320.16	47.22	160	29.5
T	308.34	345.94	37.6	170	22.1

Indiana Limestone

Sample	Mo (initial mass)	Mmax (mass of saturated sample)	Mp (Vp) Mass of pores (Mmax-Mo)	Va (apparent volume)	% porosity
1	314.28	325.77	11.49	140	8.2
3	307.85	321.47	13.62	140	9.7
B	313.64	324.86	11.22	140	8.0
C	307.84	321.84	14.0	140	10
a	309.43	322.68	15.25	140	10.9
b	306.68	320.78	14.1	140	10.1
c	309.60	323.08	13.48	140	9.6
I	307.43	321.73	14.3	140	10.2
T	304.49	318.63	14.14	140	10.1

Porosity: Post-treatment

Fort Union Brick

Sample	Mo (initial mass)	Mmax (mass of saturated sample)	Mp (Vp) Mass of pores (Mmax-Mo)	Va (apparent volume)	% porosity
1	205.07	246.34	41.27	140	29.5
2	183.21	219.74	36.53	120	30.4
B	200.27	241.02	40.75	125	32.6
C	192.34	233.48	41.14	125	32.9
a	198.43	241.72	43.29	140	30.9
b	208.20	255.55	47.35	145	32.8
c	206.09	252.30	46.21	145	32.9
I	189.89	232.63	42.74	120	35.6
T	216.14	264.64	48.50	150	32.3

New Brick

Sample	Mo (initial mass)	Mmax (mass of saturated sample)	Mp (Vp) Mass of pores (Mmax-Mo)	Va (apparent volume)	% porosity
1	309.96	321.22	11.26	140	8.0
2	267.92	277.45	9.53	110	8.7
A	345.51	359.03	13.52	150	9.0
B	294.4	304.9	10.5	125	8.4
C	247.44	256.55	9.11	100	9.1
a	326.47	338.03	11.56	150	7.8
b	323.46	334.47	11.01	140	7.7
c	260.21	270.23	10.02	110	9.1
R	335.15	346.57	11.42	140	8.2
I	326.58	338.52	11.94	140	8.5
T	292.07	303.21	11.14	120	9.3

Qualitative Salt Analysis of Test Solutions

Pre-treatment

Sample	Sulfates	Chlorides	Nitrites	Nitrates	Carbonates	Phosphates
Fort Union Brick	T	P	P	A	A	A
Paving Brick	A	T	T	A	A	A
San Juan Sandstone	T	P	P	A	A	T
Indiana Limestone	T	T	A	T	A	A

Tap water solutions

Sample	Sulfates	Chlorides	Nitrites	Nitrates	Carbonates	Phosphates
Fort Union Brick	T	Q	Q	T	A	A
Paving Brick	T	Q	A	T	A	A
San Juan Sandstone	T	Q	A	T	A	A
Indiana Limestone	T	Q	Q	T	A	A

Ethoxylated tallow amine plus tap water

Sample	Sulfates	Chlorides	Nitrites	Nitrates	Carbonates	Phosphates
Fort Union Brick	P	P	T	A	T	A
Paving Brick	P	P	A	A	T	A
San Juan Sandstone	P	P	T	A	A	A
Indiana Limestone	P	P	A	A	A	A

absence A
 small trace T
 present P
 large presence Q

Qualitative Salt Analysis of Test Solutions

Round-up[®] Manufacturer's Recommendations (17% Round-up[®])

Sample	Sulfates	Chlorides	Nitrites	Nitrates	Carbonates	Phosphates
Fort Union Brick	T	P	P	A	A	P
Paving Brick	P	P	A	A	A	P
San Juan Sandstone	T	T	T	A	A	P
Indiana Limestone	P	P	P	A	T	P

Round-up[®] Double the Manufacturer's Recommendations (34% Round-up[®])

Sample	Sulfates	Chlorides	Nitrites	Nitrates	Carbonates	Phosphates
Fort Union Brick	T	P	A	T	T	P
Paving Brick	T	P	A	T	A	P
San Juan Sandstone	T	T	P	A	A	P
Indiana Limestone	P	P	A	A	A	P

absense	A
small trace	T
present	P
large presencse	Q

Weight Change: Post-treatment

San Juan Sandstone

Sample	Pre-treatment weight (g)	Post-treatment weight (g)	Difference	Residue weight (g)	Total weight change
1	310.11	310.63	0.52	4.35	-3.83
2	261.50	261.48	-0.02	5.18	-5.2
3	278.15	279.40	1.25	3.03	-1.78
A	300.08	298.95	-1.13	1.29	-2.42
B	266.98	266.33	-0.65	0.71	-1.36
C	225.85	225.97	0.12	n/c	-0.4
a	307.72	307.38	-0.34	1.98	-2.32
b	285.23	284.49	-0.74	2.57	-3.31
c	270.92	270.82	-0.1	1.18	-1.28
R	273.62	276.17	-0.32	0.2	-0.34
I	276.49	272.99	-0.63	0.23	-0.86
T	309.27	308.40	-0.87	0.41	-1.28

Indiana Limestone

Sample	Pre treatment weight (g)	Post treatment weight (g)	Difference	Residue weight (g)	Total weight change
1	313.71	314.33	0.3	2.46	-1.84
2	309.98	310.85	0.43	2.71	-1.84
3	307.30	307.88	0.52	2.76	-2.78
A	306.01	306.06	-0.37	0.08	-0.03
B	313.63	313.65	-0.38	0.09	-0.07
C	307.77	307.84	-0.07	0.05	0.02
a	309.55	309.46	0.02	1.30	-1.39
b	304.60	306.70	-0.1	0.02	-1.95
c	309.88	309.65	-0.23	1.35	-1.58
R	307.58	311.72	-0.11	0.03	-0.18
I	311.94	307.43	-0.35	0.02	-0.24
T	306.80	304.47	-0.39	1.85	-0.15

Weight Change: Post-treatment

Fort Union

Sample	Pre treatment weight (g)	Post treatment weight (g)	Difference	Residue weight (g)	Total weight change
1	202.39	205.04	2.65	1.00	1.65.
2	181.00	183.21	2.21	0.49	1.72
3	197.71	189.79	1.08	0.26	0.82
A	176.35	176.46	0.11	0.04	-0.07
B	200.12	200.27	0.15	0.13	-0.02
C	192.10	192.31	0.21	0.11	-0.1
a	197.05	198.42	1.35	0.39	0.96
b	206.93	208.23	1.3	0.53	0.77
c	204.93	206.06	1.13	0.49	0.64
R	190.15	188.50	-0.11	.02	-0.13
I	188.61	189.88	-0.29	.02	-0.29
T	216.23	216.14	-0.09	.02	-0.11

Paving Brick

Sample	Pre treatment weight (g)	Post treatment weight (g)	Difference	Residue weight (g)	Total weight change
1	309.69	309.99	0.62	0.02	0.28
2	267.48	267.91	0.87	n/c	0.43
3	259.49	260.01	0.58	0.01	0.51
A	345.95	245.58	0.05	n/c	-0.37
B	294.78	294.40	0.02	n/c	-0.38
C	247.50	247.43	0.07	n/c	-0.07
a	326.48	326.50	-0.09	0.02	0
b	323.60	360.23	-0.1	n/c	-0.1
c	260.46	335.21	-0.23	n/c	-0.23
R	325.52	326.59	-0.15	n/c	-0.11
I	326.94	292.10	-0.22	n/c	-0.35
T	292.49	290.93	-0.13	n/c	-0.39

Hygroscopicity: Post treatment**San Juan Sandstone**

Sample	Dry weight	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Weight gain (g)
1	310.63	312.08	312.84	313.50	314.03	3.4
2	261.48	262.51	263.06	263.58	263.93	2.45
A	298.95	299.98	300.45	300.75	301.53	2.58
B	266.33	267.10	267.40	267.74	268.21	1.88
a	307.38	308.56	308.92	309.38	310.07	2.69
b	284.49	284.95	285.58	286.23	268.53	2.04
I	272.99	274.95	275.57	276.02	276.64	3.65
T	308.40	310.18	310.80	311.25	311.82	3.42

Indiana limestone

Sample	Dry weight	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Weight gain (g)
1	314.33	315.64	316.19	316.50	316.96	2.63
3	307.88	309.01	309.44	310.00	310.45	2.57
B	313.65	314.47	314.66	315.14	315.45	1.80
C	307.84	308.62	309.11	309.54	310.10	2.26
a	309.46	310.37	310.86	311.15	311.58	2.12
c	309.65	310.75	311.19	311.75	312.24	2.59
I	307.43	308.58	308.84	309.50	309.88	2.45
T	304.60	305.75	306.11	306.39	306.78	1.79

Hygroscopicity: Post treatment

Fort Union Brick

Sample	Dry weight	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Weight gain (g)
1	205.04	209.04	209.78	210.65	211.84	6.8
2	183.21	186.01	186.92	187.35	187.91	4.7
B	200.27	201.73	202.03	202.28	202.92	2.65
C	192.31	193.43	193.73	194.10	194.87	2.56
a	198.42	199.93	200.64	201.25	202.04	3.62
b	208.23	210.22	210.93	211.67	212.19	3.96
I	189.88	192.68	193.63	194.44	195.13	5.25
T	216.14	217.59	218.04	218.48	219.14	3.0

New Brick

Sample	Dry weight	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Weight gain (g)
1	309.99	311.05	311.62	312.33	312.80	2.81
2	267.91	269.08	269.00	269.77	269.77	2.38
B	294.40	294.95	295.25	295.53	295.53	1.27
C	247.43	247.73	247.77	248.06	248.06	.87
b	323.50	324.28	324.42	325.01	325.01	1.95
c	360.23	260.73	260.97	261.33	261.33	1.39
I	326.59	327.34	327.68	328.11	328.11	1.84
T	292.10	292.67	292.90	293.28	293.28	1.33

pH and Conductivity Measurements

San Juan Sandstone

Sample	pH	Conductance (μs)
1	6.78	6140
2	6.81	6630
3	6.37	6610
A	7.66	700
B	7.60	640
C	7.64	660
a	6.61	3180
b	7.09	2910
c	7.51	3070
R	8.40	1250
I	8.40	1250
T	8.26	1310
Pre-test	7.89	390

Indiana Limestone

Sample	pH	Conductance (μs)
1	6.52	5510
2	6.33	6070
3	6.65	5670
A	7.94	830
B	7.82	830
C	7.97	850
a	7.39	2880
b	7.37	3430
c	7.46	3260
R	8.19	1490
I	8.22	1530
T	8.19	1470
Pre-test	7.93	160

Fort Union

Sample	pH	Conductance (μs)
1	6.78	6140
2	6.81	6630
3	6.37	6610
A	7.66	700
B	7.60	640
C	7.64	660
a	6.61	3180
b	7.09	2910
c	7.51	3070
R	8.40	1250
I	8.40	1250
T	8.26	1310
Pre-test	7.62	430

Fresh Brick

Sample	pH	Conductance (μs)
1	4.98	5420
2	4.94	5800
3	4.93	5790
A	7.71	650
B	7.69	620
C	7.79	610
a	5.20	2850
b	5.32	2770
c	5.29	2540
R	8.27	1090
I	8.27	1090
T	8.27	1090
Pre-test	7.65	120

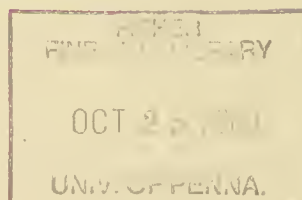
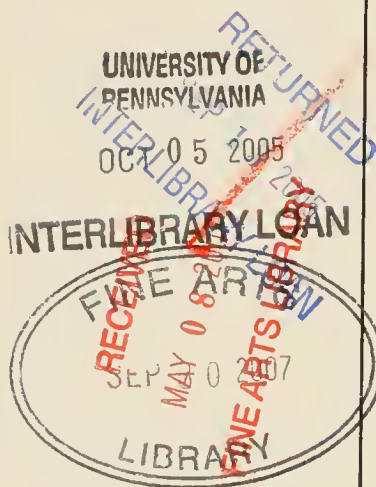
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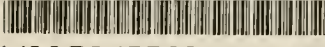
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